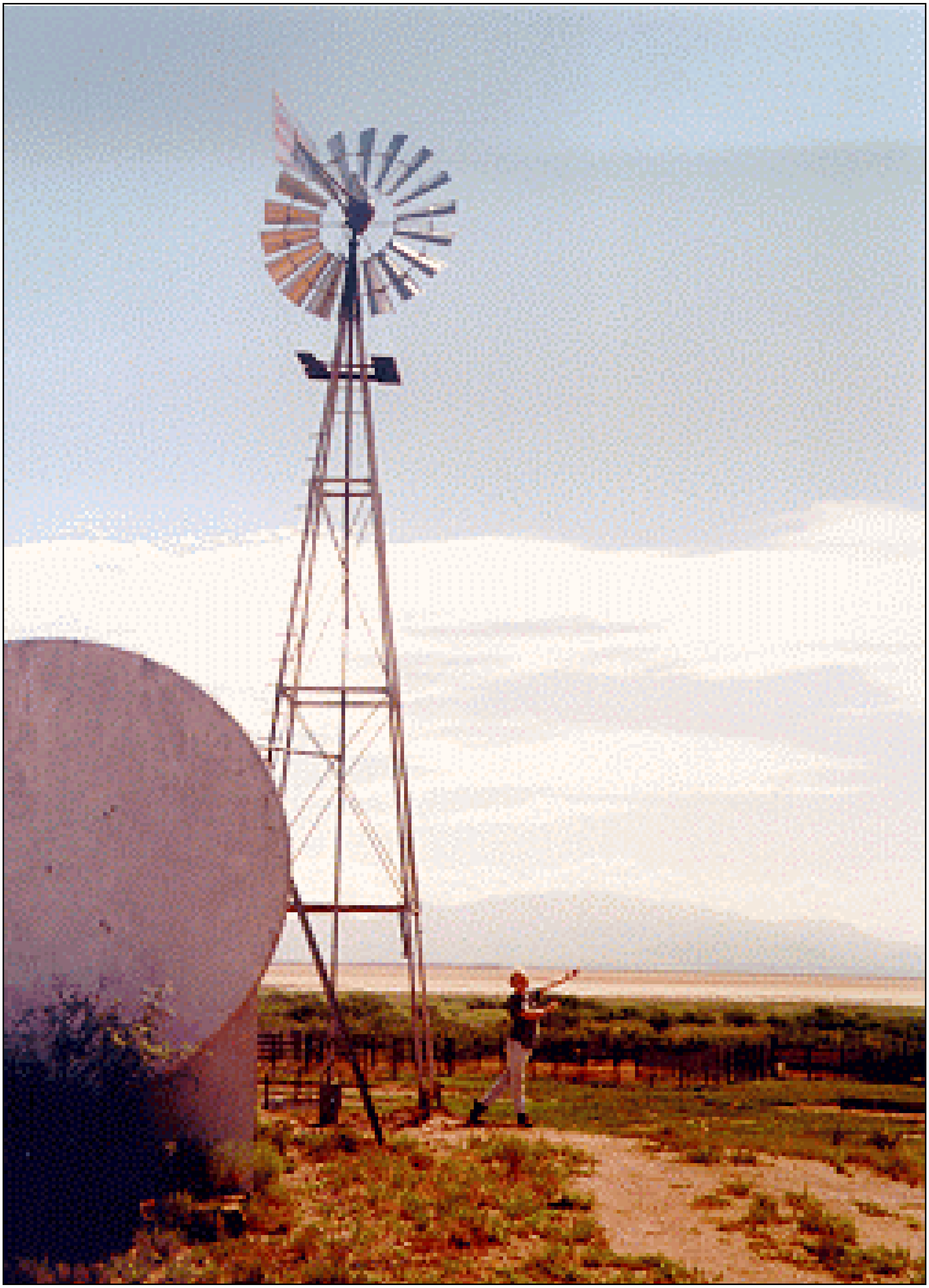

Ambient Groundwater Quality of the Willcox Basin: A 1999 Baseline Study

By Douglas C. Towne and Maureen C. Freark
Maps by Larry W. Stephenson

Arizona Department of Environmental Quality
Open File Report 2001-09
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Report Cover: A windmill, the Dos Cabezas Mountains, and an ADEQ hydrologist rise over the Willcox Playa, the lowest point in the Willcox Groundwater Basin (WGB). The playa, located in the center of the basin, is predominantly bare and covers 50 square miles. Basin floodwaters drain into the playa before evaporating. To the left of the windmill, a former underground storage tank is being used aboveground to store pumped groundwater.

Other Publications of the ADEQ Ambient Groundwater Monitoring Program

Ambient Groundwater Quality of the Lower San Pedro Basin: A 2000 Baseline Study. ADEQ Publication FS 02-09, July 2002, 4 p.

Ambient Groundwater Quality of the Lower San Pedro Basin: A 2000 Baseline Study. ADEQ Publication OFR 02-01, July 2002, 74 p.

Ambient Groundwater Quality of the Willcox Basin: A 1999 Baseline Study. ADEQ Publication FS 01-13, October 2001, 4 p.

Ambient Groundwater Quality of the Sacramento Valley Basin: A 1999 Baseline Study. ADEQ Publication FS 01-10, June 2001, 4 p.

Ambient Groundwater Quality of the Sacramento Valley Basin: A 1999 Baseline Study. ADEQ Publication OFR 01-04, June 2001, 77 p.

Ambient Groundwater Quality of the Yuma Basin: A 1995 Baseline Study. ADEQ Publication FS 01-03, April 2001, 4p.

Ambient Groundwater Quality of the Virgin River Basin: A 1997 Baseline Study. ADEQ Publication FS 01-02, March 2001, 4 p.

Ambient Groundwater Quality of the Prescott Active Management Area: A 1997-98 Baseline Study. ADEQ Publication FS 00-13, December 2000, 4 p.

Ground-Water Quality in the Upper Santa Cruz Basin, Arizona, 1998. Joint Publication: USGS Water Resources Investigations Report 00-4117 - ADEQ Publication OFR 00-06, September 2000, 55 p.

Ambient Groundwater Quality of the Douglas Basin: An ADEQ 1995-1996 Baseline Study. ADEQ Publication FS 00-08, September 2000, 4 p.

Ambient Groundwater Quality of the Prescott Active Management Area: A 1997-98 Baseline Study. ADEQ Publication OFR 00-01, May, 2000, 77 p.

Ground-Water Quality in the Sierra Vista Sub-basin, Arizona, 1996-97. Joint Publication: USGS Water-Resources Investigations Report 99-4056 - ADEQ Publication OFR-99-12, July 1999, 50 p.

Ambient Groundwater Quality of the Douglas Basin: A 1995-96 Baseline Study. ADEQ Publication OFR 99-11, June 1999, 155 p.

Ambient Groundwater Quality of the Virgin River Basin: A 1997 Baseline Study. ADEQ Publication OFR 99-4, March 1999, 98 p.

Ambient Groundwater Quality of the Yuma Basin: A 1995 Baseline Study. ADEQ Publication OFR 98-7, September, 1998, 121 p.

Collection and Analysis of Ground-Water Samples in the Sierra Vista Basin, Arizona, 1996. Joint Publication: USGS Fact Sheet FS-107-97- ADEQ Factsheet 97-8, August 1997, 4 p.

The Impacts of Septic Systems on Water Quality of Shallow Perched Aquifers: A Case Study of Fort Valley, Arizona. ADEQ Publication OFR 97-7, February 1997, 70 p.

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ABBREVIATIONS

amsl	above mean sea level
af	acre-feet
af/yr	acre-feet per year
AMA	Active Management Area
ADEQ	Arizona Department of Environmental Quality
ADHS	Arizona Department of Health Services
ADWR	Arizona Department of Water Resources
bls	below land surface
BLM	Bureau of Land Management
$CI_{0.95}$	95 percent Confidence Interval
EPA	U.S. Environmental Protection Agency
$d^{15}N$	stable isotope of nitrogen
gpm	gallons per minute
GWPL	Groundwater Protection List pesticides
LLD	Lower Limit of Detection
MCL	Maximum Contaminant Level
Fg/l	micrograms per liter
FS/cm	microsiemens per centimeter at 25E Celsius
mg/L	milligrams per liter
MRL	Minimum Reporting Level
MTBE	methyl tert-butyl ether
ns	not significant at p # 0.05
NTU	nephelometric turbidity unit
$d^{15}N$	stable isotope of nitrogen
pCi/l	picocuries per liter
QA	Quality Assurance
QAAP	Quality Assurance Project Plan
QC	Quality Control
SDWA	Safe Drinking Water Act
SC	Specific Conductivity
SU	standard pH units
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
USGS	U.S. Geological Survey
VOC	Volatile Organic Compound
WCX	Prefix for specific groundwater samples collected in the WGB
WGB	Willcox Groundwater Basin

“Although peatland classification is evolving, taxonomy has historically been based on hydrology or water chemistry. Peatlands have been most commonly classified from ombrotrophic, where precipitation serves as the only source of nutrients, to minerotrophic, where both precipitation and mineral rich groundwater provide nutrients. Bogs are strongly ombrotrophic peatlands where precipitation is the dominant source of hydrology; these have low nutrient concentrations, are mostly acidic, and have low species diversity. Alternatively, fens are minerotrophic peatlands that have significantly mineral rich–often flowing–groundwater inputs, and these have higher species diversity due to more available nutrients and higher pH.”

Matthew J. Barry
Former ADEQ Watershed Coordinator
--writing on the importance of groundwater inputs to species diversity in fens in--

Plant Community Development in Two Minerotropic Peatlands [8]

Visit the ADEQ Ambient Groundwater Monitoring Program at:

http://www.adeq.state.az.us/environ/water/assess/ambient.html#studies

http://www.adeq.state.az.us/environ/water/assess/target.html#studies

Ambient Groundwater Quality of the Willcox Basin:
A 1999 Baseline Study

By Douglas C. Towne and Maureen C. Freark

Abstract - A baseline groundwater quality study of the Willcox Groundwater Basin (WGB) was completed by the Arizona Department of Environmental Quality (ADEQ) in 1999. Groundwater is the main water supply in this semiarid basin, which is located in Cochise and Graham Counties in southeastern Arizona. The basin is surrounded by topographically higher areas so that most drainage is internal and flows to the Willcox Playa, an alkali flat in the central portion of the basin. For the study, 58 groundwater sites - 46 random sites and 12 targeted sites - were sampled for inorganic constituents. Varying numbers of sites were also sampled for Volatile Organic Compounds (VOCs)(54 sites), radiochemicals (44 sites), nitrogen isotopes (7 sites), and pesticides (4 sites).

Thirty-six (36) percent of the sample sites had concentrations of at least one constituent that exceeded a health-based, federal or state water-quality standard. These are enforceable standards which define the maximum concentration of a constituent allowed in a public water system.[48] Constituents exceeding these standards include antimony (1 site), arsenic (3 sites under current standards, 9 sites under standards due to become effective in 2006), fluoride (8 sites), nitrate (5 sites), gross alpha (8 sites), and radium-226+228 (1 site). Forty (40) percent of the sample sites had concentrations of at least one constituent that exceeded an aesthetics-based, federal water quality guideline. These unenforceable guidelines define the maximum concentration of a constituent that can be present without unpleasant taste, color, odor, or other aesthetic effect on drinking water.[48] Constituents exceeding these guidelines include chloride (2 sites), fluoride (13 sites), iron (1 site), manganese (1 site), pH (4 sites), sulfate (4 sites), and total dissolved solids or TDS (11 sites). At one site, VOCs were detected that are common by-products of chlorination.[34] No pesticides or related degradation by-products were detected. Although water quality constituent exceedances occurred throughout the basin, they were largely concentrated in four areas: near the Spike E Hills northeast of the city of Willcox (fluoride, arsenic, and pH); areas of granitic rock (gross alpha); northwest of the Sulphur Hills (nitrate, fluoride, and sulfate); and immediately west of the Willcox Playa (chloride and sulfate). The study results suggest that, apart from these areas, groundwater appears to be largely suitable for domestic uses.

Groundwater in the WGB is generally *fresh*, *slightly alkaline*, and varies widely in hardness concentrations. The chemistry is typically *calcium-bicarbonate* except near the Willcox Playa (*sodium-mixed anion*) and northwest of the Sulphur Hills (*calcium-sulfate*). Twenty-five (25) percent of sites had nitrate (as nitrogen) concentrations (> 3 milligrams per liter) which may indicate impacts from human activities.[31] Analyses were conducted on 18 trace elements; only boron, chromium, fluoride, and zinc were detected at more than 10 percent of sample sites.

Groundwater quality varied significantly by aquifer, geology, geographic location, and with groundwater depth. Constituents such as nitrate, pH, potassium, and temperature were higher in the *alluvial aquifer* than in *hardrock areas*. Sodium and chloride were higher in *young alluvium* near the Willcox Playa than in *old alluvium*. Gross alpha was higher in groundwater associated with *granite rock* than in *old* and *young alluvium*. Bicarbonate, calcium, hardness, and sulfate were higher in the southern portion of the basin than in the northern portion (Kruskal-Wallis test, p # 0.05). Many constituents such as bicarbonate, calcium, chloride, gross alpha, hardness, sodium, sulfate, TDS, and total Kjeldahl nitrogen decreased with increasing groundwater depth below land surface (bls) (regression analyses, p # 0.05). TDS and some major ions attained a *critical level* at approximately 110 feet bls. These constituent levels remained generally constant at groundwater depths greater than the *critical level* but were highly variable and sometimes dramatically higher at depths shallower than 110 feet bls. Although only limited time-trend analyses were conducted for this study, constituents in most areas of the basin appear to be controlled by natural geochemical reactions and would probably not vary significantly in the short term. An exception may occur near Kansas Settlement, a farming community located southeast of the Willcox Playa. Targeted sampling conducted indicates that shallow groundwater quality is probably impacted by a variety of sources, especially irrigation recharge carrying salts and nitrate.

INTRODUCTION

The Willcox Groundwater Basin (WGB), located in southeastern Arizona, is a largely rural landscape with scattered small settlements. Historically, farms were located where fertile soil occurred in the valley (**Figure 1**), and ranches were found in upland tracts and areas of poor soil. Recent population increases are largely the result of dispersed residential development occurring throughout the basin. Groundwater is the primary source in the WGB for domestic, municipal, irrigation, livestock, and mining uses. In the coming decades, population in the WGB is expected to continue to gradually increase, and this additional development raises several groundwater quality issues. Are there areas where groundwater does not currently meet U.S. Environmental Protection Agency (EPA) Safe Drinking Water Act (SDWA) water quality standards? Will the increased development impact groundwater quality?

To assess these hydrological questions, the Arizona Department of Environmental Quality (ADEQ) Groundwater Monitoring Unit designed a study to characterize the current (1999) groundwater quality conditions in the WGB. Sampling by ADEQ was completed as part of the Ambient Groundwater Monitoring Program, which is based on the legislative mandate in the Arizona Revised Statutes §49-225 that authorizes[3]:

"*...ongoing monitoring of waters of the state, including...aquifers to detect the presence of new and existing pollutants, determine compliance with applicable water quality standards, determine the effectiveness of best management practices, evaluate the effects of pollutants on public health or the environment, and determine water quality trends.*"

This ADEQ program examines regional groundwater quality in Arizona groundwater basins such as the WGB. Groundwater sample sites are chosen using a systematic grid-based, random selection process. The analytical results of these samples are compared to water quality standards and statistically examined for significant patterns and relationships.

Purpose and Scope

ADEQ collected samples from 58 sites for this groundwater quality assessment of the WGB. Types and numbers of samples collected and analyzed include inorganics (physical parameters, major ions, nutrient constituents, and trace elements) (58 sites), Volatile Organic Compounds (VOCs) (54 sites), radiochemistry (52 sites), isotopes of nitrogen (7 sites) and Groundwater Protection List (GWPL) pesticides (4 sites).

Figure 1. A center pivot irrigates a cotton field in the Stewart District as the Winchester Mountains loom in the background. Crop production in this area north of Willcox Playa is aided by low groundwater salinity levels.

Aspects of Study - Several groundwater quality concerns are examined in this report:

- Current (1999) groundwater quality conditions on a regional scale.
- Variation in groundwater quality among aquifers, geology, geographic location, and with groundwater depth.

- Relationships among groundwater quality constituents.

- Groundwater quality changes between 1979, 1990, and 1999.

Reasons for Study - The WGB was selected for study for the following reasons:

- Support the ADEQ watershed program by expanding the hydrologic information available on the San Pedro Watershed. County and local governments can also benefit from this study.

- Add to groundwater quality data available for the WGB, a lack of which was noted in an ADEQ report.[28]

- Recent population growth and a subsequent increase in the number of wells provide greater access to investigate groundwater.

Benefits of Study - This groundwater quality study was undertaken with the purpose of developing a reproducible, scientific report utilizing statistical analysis. The report's conclusions concerning groundwater quality is anticipated to provide the following four benefits:

#1 - Many rural residents in the WGB obtain domestic supplies from private wells whose water is seldom tested for a wide variety of possible pollutants. Arizona statutes only require well drilling contractors to disinfect, for potential bacteria contamination, new wells which are used for human consumption. Many wells are not tested for other groundwater quality concerns. Thus, contamination affecting groundwater pumped from private wells may go undetected for years and have adverse health effects on users of this resource. Testing all private wells for a wide variety of groundwater quality concerns would be prohibitively expensive. An affordable alternative is this type of statistically-based groundwater study characterizing regional groundwater quality conditions and identifying areas with impaired groundwater conditions.

#2 - A process for evaluating potential groundwater quality impacts arising from a variety of sources including natural mineralization, mining, agriculture, livestock, septic tanks, and poor well construction.

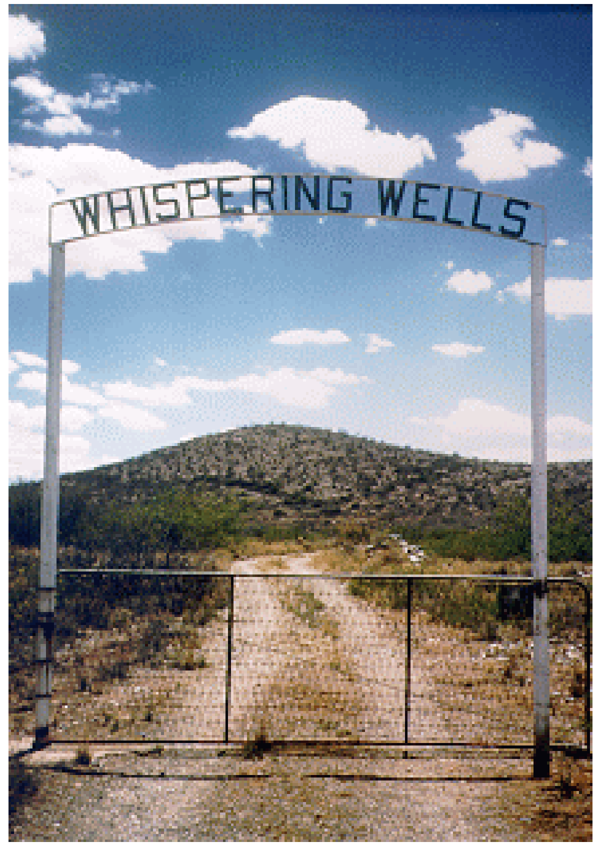


Figure 2. Upland areas of the basin, such as this gateway to the Dos Cabezas Mountains, are indeed the land of *whispering wells* with many low-production, shallow windmills supplying water for stock use. However in valley areas, the silence is often broken by high-production irrigation wells powered by deafening diesel pumps.

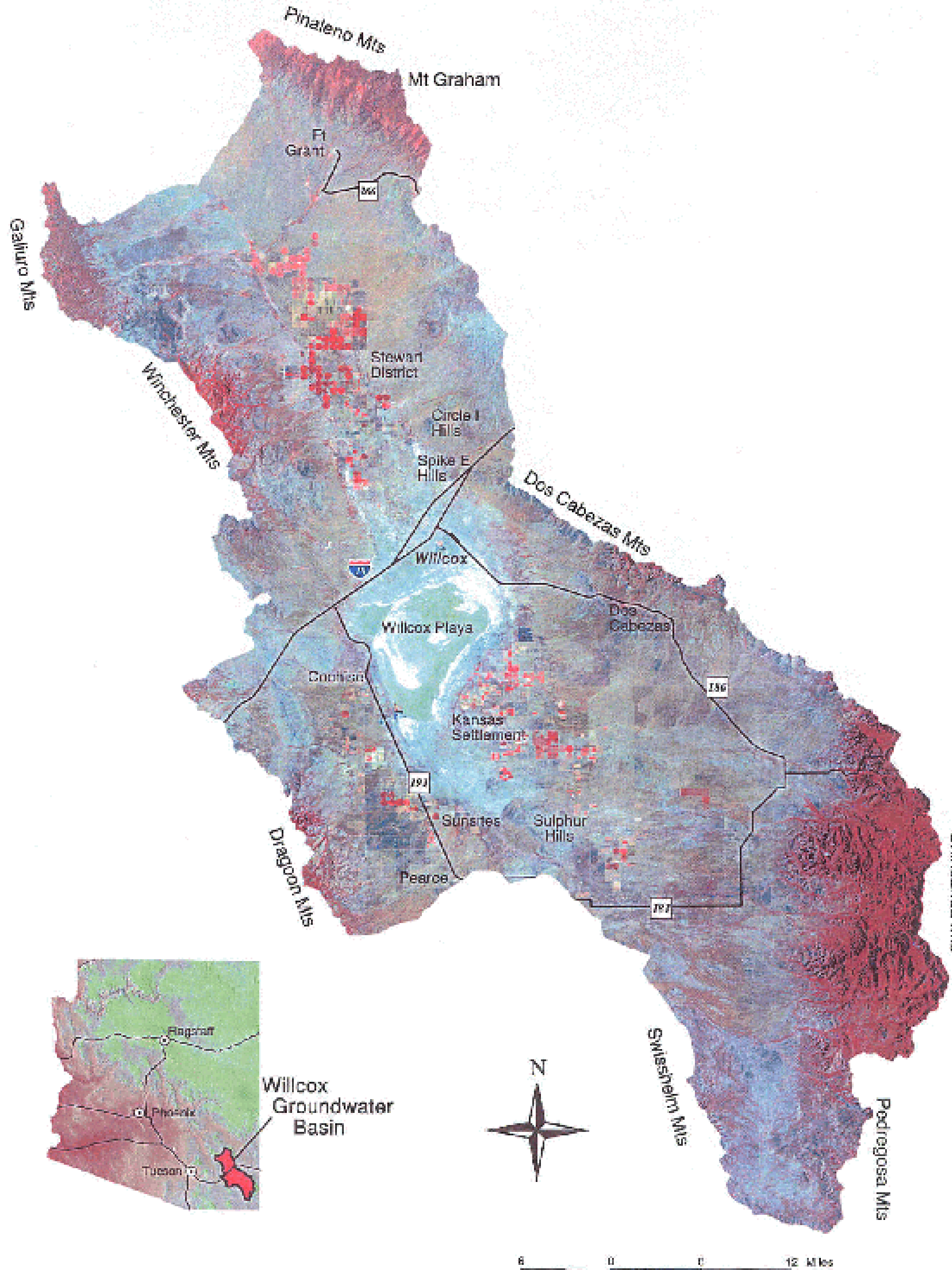
#3 - A process for evaluating the effectiveness of groundwater protection efforts such as aquifer protection permits and best management practices by tracking groundwater quality changes.

#4 - A process for identifying future locations of public supply wells and wellhead protection areas.

Physical Setting

The WGB is located roughly 80 miles east of the city of Tucson and includes portions of Cochise and Graham Counties (**Figure 3**). The basin is about 90 miles long and varies from 10 to 30 miles wide, comprising approximately 1,911 square miles.[35] The WGB occupies the northern part of the Sulphur Springs Valley, which is a large northwest-trending intermontane trough that extends from northeastern

Figure 3 - Willcox Groundwater Basin



Sonora, Mexico to the headwaters of Aravaipa Creek.[11] The Sulphur Springs Valley is located within the Basin and Range Lowlands province, which consists of northwest-trending alluvial basins separated by elongated fault-block mountain ranges.

Topography - The WGB is characterized by three major topographic features:

- Mountains,
- Stream-built slopes, and
- Playa flat.[11]

Various mountain ranges form the boundaries of the WGB: to the northeast are the Pinaleno Mountains; to the east the Dos Cabezas and Chiricahua Mountains; to the south are the Pedregosa and Swisshelm Mountains and Squaretop Hills; and to the west are the Dragoon, Little Dragoon, Winchester, and Galiuro Mountains.[6] Elevations in the basin range from 10,717 feet above mean sea level (amsl) at Mount Graham in the Pinaleno Mountains to approximately 4,130 feet amsl at the Willcox Playa. The mountain ranges on the east side of the basin are larger and higher than those on the west. The alluvial slopes are steepest near the mountains and become much flatter toward the Willcox Playa.[11] Lands near the playa are commonly cultivated but there are areas of saline-alkali affected soils that may not be suitable for agriculture.[36]

Surface Water - Surrounded by topographically higher areas, most drainage in the WGB is internal and flows to the Willcox Playa in the center of the basin. The Whitewater Draw in the extreme southern portion of the basin is the only exception, draining into the adjacent Douglas Basin.[35] The pork-chop shaped Willcox Playa, comprising approximately 50 square miles, is nearly devoid of vegetation. This alkali flat acts as an evaporation dish for floodwaters and is a remnant of the much larger, Pleistocene-age Lake Cochise.[35]

Surface water from rain and snowmelt moves from mountain fronts onto the gently sloping alluvial valley floor and toward the Willcox Playa. As the surface flow is attenuated by seepage and evaporation, the accompanying sediment load is deposited. Streamflow usually completely infiltrates before reaching the Willcox Playa.[11] The majority of streams within the WGB are ephemeral and flow only in response to precipitation events; however, four stream reaches originating on Mount Graham or Chiricahua Peak have perennial stretches within the basin. These streams and the length of their perennial reaches include Grant Creek (10 miles), Rucker Canyon (7 miles), Turkey Creek (5 miles), and Rock Canyon (3 miles).[6]

Climate - Although varying with elevation, the climate in the WGB is generally semiarid and is characterized by hot summers and cool, moderate winters. Precipitation typically occurs during two periods: as intense rains of short duration produced by thunderstorms from July to September and as gentle, long duration rains and some snow produced by frontal-type storms during the winter months.[35] May is the driest month while July and August are the wettest months. Annual precipitation averages 11 inches near the community of Cochise, increasing to over 18 inches at higher elevations such as at Chiricahua National Monument.[35] Snow is minimal (1 - 4 inches) on the valley floor but averages over 13 inches in the surrounding mountains. The average annual air temperature is 60^0 - 62^0 Fahrenheit, though temperature extremes of 114^0 Fahrenheit and -10^0 Fahrenheit have been recorded.[35] The frost-free season ranges between 175 - 200 days.[36]

Cultural Setting

The WGB is partially surrounded by the Coronado National Forest, with the central portion primarily composed of private land and State Trust land. The city of Willcox, located by the playa, is the population center of the basin. Willcox has experienced gradual growth in the latter part of the 20th century, increasing in population from 2,568 in 1970 to 3,122 in 1990.[35] Presently, Willcox serves as a regional agricultural, service, trade, and transportation center. Other settlements within the basin include Bonita, Fort Grant, and Sunset in the northern portion of the basin while Cochise, Dos Cabezas, Kansas Settlement, Pearce, and Sunsites are located in the southern portion.

Historical Development - Livestock grazing was the chief economic activity from the late 1860s, when ranchers first entered the area, until around 1950.[35] Willcox began as a regional service and livestock shipping center in 1880, when the main line of the Southern Pacific Railroad reached the basin.
With the advent of mining in the surrounding mountain areas, especially near the communities of

Pearce and Dos Cabezas, a need developed for locally produced agricultural and dairy products.[35]
Dry and flood-water farming were the initial methods used by settlers to irrigate crops in the WGB. To augment these unreliable water sources, around 57 irrigation wells, typically located in areas of shallow groundwater in the north-central part of the basin, were constructed by 1910.[33] These irrigation wells were constructed by digging an open pit to within a foot of the water table at which point a hand-augered hole was extended to the water-bearing strata. Energy was provided by a horizontal centrifugal pump set into the pit and driven by a belt from a gasoline engine at the surface.[33]

These early wells were supplemented in the 1930s by deep-well turbine pumps that enabled an associated increase in the production of irrigated crops. As electric power became available in the early 1950s, irrigated agriculture became the leading industry in the basin.[35] The amount of land irrigated peaked during the early 1980s (**Figure 4**) before decreasing due to rising energy costs.[44] Advances in irrigation technology and the planting of new orchard crops have again increased acreage irrigated in the WGB during the 1990s. The three major areas of irrigated crop production are the Stewart District located northwest of Willcox, the Kansas Settlement District located southeast of the playa, and the Cochise-Pearce District that stretches between these two towns.[44]

Figure 4. A rusting natural gas turbine pump and a formerly irrigated field cover in tumbleweeds were a common landscape feature in the early 1980s after increased energy costs idled large tracts of farmland in the WGB.

GEOHYDROLOGY

Geology

The WGB is a long, broad valley formed by large-scale faulting and the subsequent uplifting and eroding of the surrounding mountain blocks during the Middle to Late Tertiary period.[35] The mountains rise abruptly from beneath the alluvium that forms the valley floor and are composed of older rocks. These range in age from Precambrian through Tertiary and have been uplifted, structurally deformed, and dissected by stream erosion.[11] These forces have left a rugged mountain topography of great relief, steep slopes, and deep canyons. As the igneous, metamorphic, and sedimentary rocks of the adjacent mountains eroded, this debris filled the valley that has been without external surface drainage throughout most of its geologic history.[14]

These debris deposits, in ascending order, are consolidated and unconsolidated alluvium and have a maximum thickness in the central part of the valley of approximately 6,400 feet.[11] The consolidated alluvium has been subdivided into moderately consolidated alluvium of Tertiary age (consisting of conglomerate, sandstone, and mudstone) and poorly consolidated alluvium of Tertiary-Quaternary age (consisting of poorly cemented lenticular beds of sand, gravel, silt, and clay).[35] The unconsolidated alluvium (of Quaternary age) has been subdivided into stream deposits consisting of lenticular interbedded gravel, sand, silt, and clay, and lake-bed deposits consisting of clay and silt, locally overlain by thin beach gravel and sand dunes.[11]

Aquifers

Groundwater in the WGB is principally found in the unconsolidated alluvial deposits of the Sulphur Springs Valley and consist of both stream and lake-bed deposits.[11] Two other limited sources of groundwater in the basin include the consolidated alluvial deposits as well as the igneous, metamorphic, and sedimentary rocks that form the surrounding mountains.

Stream Deposits - The most productive water-bearing unit are stream deposits which may produce up to 2,000 gallons per minute (gpm).[32] The stream deposits are composed of gravel, sand, silt, and clay and may be separated by impermeable silt and clay.[35] Irrigation wells in the Stewart District typically obtain their water from the stream deposits while those in the Kansas Settlement District obtain water from both the unconsolidated alluvium and the underlying consolidated alluvium. As such, aquifer materials penetrated near Kansas Settlement (**Figure 5**) are more homogeneous but much less permeable than in the Stewart District.[11]

Lake Bed Deposits - These deposits, consisting mainly of clay materials, outcrop near the Willcox Playa and are interbedded with the stream deposits at depths of 200-300 feet bls in other parts of the WGB.[35] Near the playa, these fine-grained sediments act as a confining layer to the water in the underlying stream deposits creating localized artesian conditions. Flowing wells have been drilled on the north and east sides of the playa.[11]

Perched Groundwater - Perched groundwater conditions may occur where coarse-grained stream deposits are underlain by lake bed deposits.[6] The lake bed deposits form a relatively impermeable layer that impedes the downward percolation of water in and around the playa, forming a shallow groundwater zone in the area. The relatively shallow depths to groundwater found in the vicinity of the Willcox Playa are clearly in contrast to the greater groundwater depths in the regional aquifer.[35]

This perched groundwater zone is clearly defined on the east and south sides of the playa, while the shallow groundwater zone to the north and west appears to grade into the regional aquifer making the boundary indistinct.[35] Depth to groundwater in the shallow groundwater zone in the vicinity of the Willcox Playa ranges from 13 feet bls to 107 feet bls.[35]

Consolidated Alluvium - Groundwater also occurs in the older, consolidated alluvium that underlies the unconsolidated alluvium. The poorly to moderately cemented deposits of the consolidated alluvium exhibit very low to moderate permeability; however, large quantities of water may be obtained if a sufficient thickness of saturated material is penetrated by a well.[11]

Hardrock Areas - The igneous, metamorphic, and sedimentary rocks that form the surrounding mountains generally does not yield more than a few gpm to springs and wells for domestic and livestock uses.[35] Groundwater may occur within thin alluvial deposits overlying the bedrock as well as within the weathered and fractured zones in the bedrock. The water-bearing characteristics of the bedrock are largely dependent on the amount of fractures.[32]

Hardrock areas include the Chiricahua, Dos Cabezas, Dragoon, Galiuro, Little Dragoon, Pedregosa, Pinaleno, Swisshelm, and Winchester Mountains as well as minor outcrops such as the Circle I, Gunnison, Pat, Red Bird, Squaretop, and Sulphur Hills.

Figure 5. An irrigation well in the Kansas Settlement is framed in the foreground by discharge pipe and in the background by the Dos Cabezas Mountains.

Groundwater Characteristics

Groundwater Storage and Recharge - The WGB has an estimated 45 million acre-feet (af) of groundwater in storage to a depth of 1,200 feet bls.[6] Natural recharge is estimated at approximately 15,000 acre-feet per year (af/yr). Recharge occurs predominantly by subsurface inflow from the surrounding mountains and infiltration of surface water on alluvial fans around the margin of the valley.[11] A few streams are perennial along limited stretches in the mountains but generally disappear past the mountain front alluvial-fan contact as they traverse the fan's permeable deposits.

Surface flow from intense precipitation, rapid snowmelt, or a combination of both, can reach the playa, but the majority of this water is lost by evaporation prior to recharging the aquifer. If the playa surface is dry and water flows onto the playa, an initial pulse of water may recharge the perched aquifer by flowing down cracks formed in the dry playa sediments (**Figure 6**). However, after initial wetting, the fine-grained sediments swell quickly, preventing any further downward flow. The remaining water stands on the playa surface until it evaporates.[43]

Seepage from irrigation water also contributes recharge to the regional aquifer in heavily pumped agricultural areas. Due to high evapotranspiration rates, little or no recharge is believed to result from direct precipitation,[11] though other sources indicate that much of the annual recharge may occur along the valley floor.[40]

Figure 6. Tamarisk have sprouted in a rill in the barren expanse of the Willcox Playa; the Sulphur Hills are in the background. During wet periods, floodwaters cover the playa creating a large, temporary lake utilized a wide variety of migratory wildfowl including sandhill and whooping cranes.

Groundwater Use - Groundwater is discharged from the WGB primarily by artificial means (groundwater pumping), though natural outflow also occurs both southward to the Douglas Basin and northward to the Aravaipa Basin.[35] Discharge also occurs through evapotranspiration by phreatophytic vegetation in shallow groundwater areas surrounding the playa.

The majority of groundwater pumped in the WGB is used for irrigation. Withdrawals averaged about 1,000 af between 1915 and 1940, exceeded 100,000 af in 1954, averaged 300,000 af/yr between 1967 and 1975, and dipped in the 1980s, averaging about 100,000 between 1980 and 1988.[35] Discharge measurements of irrigation wells have been reported as high as 2,199 gpm.[35]

Groundwater Depth - Predevelopment groundwater depths were greatest near the mountain fronts and shallowest near the Willcox Playa.[11] Depth to groundwater ranged from 34 feet below land surface (bls) to 649 feet bls in the regional aquifer with water levels in some wells declining by more than 200 feet between 1954 and 1970.[32] With the decrease in irrigated acreage in the late 1970s, water levels have typically risen in formerly heavily pumped areas while some wells outside the major pumping areas experienced declining water levels.[35]

Groundwater Movement - The direction of groundwater movement in the WGB prior to extensive groundwater development in the basin was from the perimeter of Sulphur Springs Valley toward the Willcox Playa and possibly south toward the Douglas basin, mirroring surface water drainage.[6] Large-scale withdrawal of groundwater has significantly altered the direction of groundwater movement toward several agricultural areas on the valley floor. Four groundwater level depressions have formed in the Kansas Settlement area, the Stewart District northwest of Willcox, an area north of Pearce, and an area southwest of Cochise.[35]

GROUNDWATER SAMPLING RESULTS

To characterize the regional groundwater quality of the WGB, ADEQ personnel sampled 58 groundwater sites consisting of 53 wells and 5 springs (**Figure 7**). Of the 58 sample sites, 46 sites were randomly-selected using a grid-based overlay and 12 sites were targeted in specific areas. Information on locations and characteristics of groundwater sample sites is provided in **Appendix A**. Varying numbers of sites were sampled for the following types of samples:

- 58 inorganic sites,
- 54 VOC sites,
- 44 radiochemical sites,
- 7 nitrogen isotope sites, and
- 4 GWPL pesticide sites.

Water Quality Standards/Guidelines

As an environmental regulatory agency, the most important determination ADEQ makes concerning the collected samples is comparing their analytical results with various water quality standards. Three sets of drinking water standards that reflect the best current scientific and technical judgment available on the suitability of water for drinking were used to determine the suitability of these groundwater sites for domestic purposes:

- Federal Safe Drinking Water Act (SDWA) **Primary Maximum Contaminant Levels** (**MCLs**). These health-based standards define the maximum concentration of a constituent allowed in water supplied by a public-water system.[48]

- State of Arizona **Aquifer Water Quality Standards** apply to aquifers that are classified for drinking water use.[3] All aquifers within Arizona are currently classified for drinking water use. These State standards, found in Arizona Administrative Code R18-11-401, are almost identical to the federal Primary MCLs.
- Federal SDWA **Secondary MCLs**. These are aesthetics-based, unenforceable guidelines that define the maximum concentration of a constituent that can be present without unpleasant taste, color, odor, or other aesthetic effect on drinking water.[48]

Water Quality Standard/Guideline Exceedances

Health-based Primary MCL water quality standards and State aquifer water quality standards were exceeded at 21 of 58 sites (**Figure 7**). Constituents above Primary MCLs include antimony (1 site), arsenic (3 sites under current standards, 9 sites under standards due to become effective in 2006), fluoride (8 sites), nitrate (5 sites), gross alpha (8 sites), and radium-226 plus radium-228 (1 site) (**Table 1**). One site also exceeded the proposed Primary MCL for uranium.

Aesthetics-based Secondary MCL water quality guidelines were exceeded at 23 of 58 sites (**Figure 7**). Constituents above Secondary MCLs include chloride (2 sites), fluoride (13 sites), iron (1 site), manganese (1 site), pH (4 sites), sulfate (4 sites), and TDS (11 sites) (**Table 2**).

Analytical Results

Analytical inorganic and radiochemistry results of the 46 randomly collected sample sites are summarized in **Table 3**. This table contains the following constituent concentration information:

- Minimum reporting levels (MRLs),
- Number of sample sites over the MRL,
- Upper and lower 95 percent confidence intervals ($CI_{95\%}$), and
- Mean.

Confidence intervals are a statistical method which indicates that 95 percent of a constituent's population lies within a stated confidence interval. For example, if 100 additional sites were sampled in the WGB, the constituent concentrations for 95 sites would be expected to fall within the 95 percent confidence intervals. This statistical index is useful for evaluating targeted sites by identifying constituent concentration outliers that may be produced by groundwater quality impacts from specific facilities and/or land uses. Specific constituent information for each groundwater site is found in **Appendix B**.

Figure 7 - Water Quality Exceedances and Sampling Sites

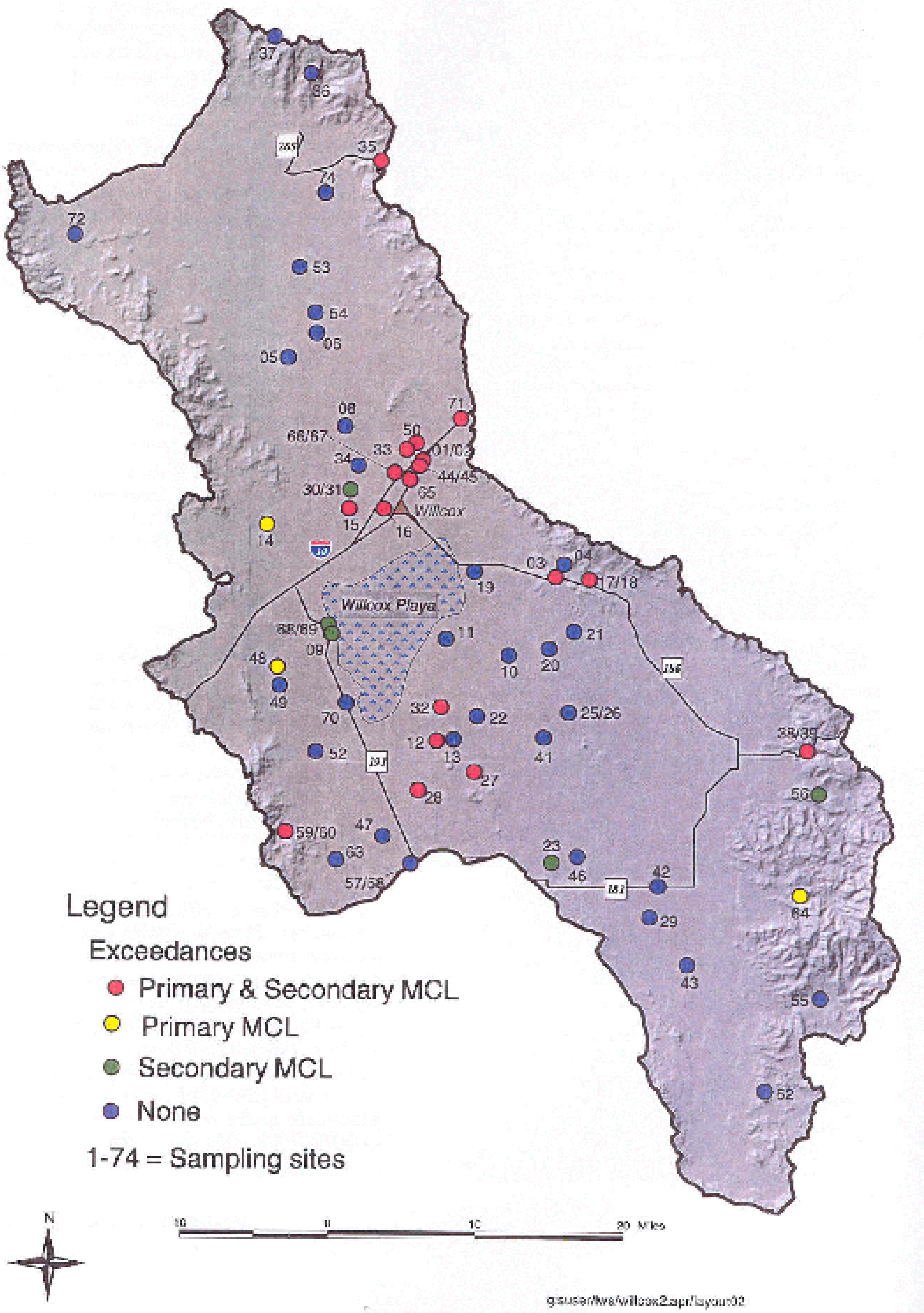


Table 1. WGB Sites Exceeding Health-Based Water Quality Standards (Primary MCLs)

Constituent	Primary MCL	Sites Exceeding Primary MCLs	Concentration Range of Exceedances	Health Effects
		Nutrients		
Nitrite (NO_2-N)	1.0	0	--	Methemoglobinemia
Nitrate (NO_3-N)	10.0	5	12 - 18 mg/l	Methemoglobinemia
		Trace Elements		
Antimony (Sb)	0.006	1	0.0090 mg/l	Cancer
Arsenic (As)	0.05 0.01*	3 9	0.065 - 0.74 mg/l 0.01 - 0.74 mg/l	Dermal and nervous system toxicity
Barium (Ba)	2.0	0	--	Circulatory system damage
Beryllium (Be)	0.004	0	--	Bone and lung damage
Cadmium (Cd)	0.005	0	--	Kidney damage
Chromium (Cr)	0.1	0	--	Liver and kidney damage
Fluoride (F)	4.0	8	4.0 - 10.0 mg/l	Skeletal damage
Mercury (Hg)	0.002	0	--	Central nervous system disorders; kidney damage
Nickel (Ni)	0.1	0	--	Heart and liver damage
Selenium (Se)	0.05	0	--	Gastrointestinal damage
Thallium (Tl)	0.002	0	--	Gastrointestinal damage; liver, kidney, and nerve damage
		Radiochemistry Constituents		
Gross Alpha (piC/l)	15	8	15 - 239 piC/l	Cancer
Ra-226+228 (piC/l)	5	1	27.2 piC/l	Bone cancer
Uranium (Fg/l)	20 - 80 proposed	1	232 Fg/l	Cancer

All units are mg/l except where noted with radiochemical constituents
* new arsenic primary MCL scheduled to be implemented in 2006
Source [48]

Table 2. WGB Sites Exceeding Aesthetics-Based Water Quality Standards (Secondary MCLs)

Constituents	Secondary MCL	Sites Exceeding Secondary MCLs	Concentration Range of Exceedances	Aesthetic Effects
Physical Parameters				
pH - field (su)	6.5 to 8.5	4	8.60 - 9.76 su	Corrosive water
General Mineral Characteristics				
TDS	500	11	500 - 2100 mg/l	Unpleasant taste
Major Ions				
Chloride (Cl)	250	2	260 - 290 mg/l	Salty taste
Sulfate (SO_4)	250	4	260 - 1000 mg/l	Rotten-egg odor, unpleasant taste, and laxative effect
Trace Elements				
Fluoride (F)	2.0	13	2.1 - 10 mg/l	Mottling of teeth enamel
Iron (Fe)	0.3	1	0.42 mg/l	Rusty color, reddish stains, and metallic tastes
Manganese (Mn)	0.05	1	0.14 mg/l	Black oxide stains and bitter, metallic taste
Silver (Ag)	0.1	0	--	Skin discoloration and greying of white part of eye
Zinc (Zn)	5.0	0	--	Metallic taste

All units are mg/l except where noted with pH (standard units)
Source[26 48]

Table 3. Summary Statistics for WGB Random Data

Constituent	Minimum Reporting Limit (MRL)	Number of Samples Over MRL	Lower 95% Confidence Interval	Mean	Upper 95% Confidence Interval
Physical Parameters					
Temperature (°C)	N/A	46	20.4	21.6	22.8
pH-field (SU)	N/A	46	7.4	7.56	7.72
Turbidity (NTU)	0.01	46	0.41	1.18	1.96
General Mineral Characteristics					
Total Alkalinity	2.0	46	133	155	176
Phenol. Alkalinity	2.0	4	>90% of data below MRL		
SC-lab (FS/cm)	N/A	46	408	526	644
Hardness	10.0	45	139	176	213
TDS	10.0	46	260	330	400
Major Ions					
Calcium	5.0	45	43	54	65
Magnesium	1.0	45	7.8	11.2	14.6
Sodium	5.0	45	29	43	56
Potassium	0.5	45	1.6	1.9	2.3
Bicarbonate	2.0	46	162	189	215
Carbonate	2.0	4	>90% of data below MRL		
Chloride	1.0	46	14.7	31.4	48.1
Sulfate	10.0	33	28	53	78
Nutrients					
Nitrate (as N)	0.02	44	1.4	2.7	3.9
Nitrite (as N)	0.02	0	>90% of data below MRL		
Ammonia	0.02	0	>90% of data below MRL		
TKN	0.05	22	0.05	0.07	0.09
Total Phosphorus	0.02	4	>90% of data below MRL		

All units mg/l except where noted with physical parameters
Source [37]

Table 3. Summary Statistics for WGB Random Data--Continued

Constituent	Minimum Reporting Limit (MRL)	Number of Samples Over MRL	Lower 95% Confidence Interval	Mean	Upper 95% Confidence Interval
Trace Elements					
Antimony	0.005	0	>90% of data below MRL		
Arsenic	0.01	4	>90% of data below MRL		
Barium	0.1	5	>90% of data below MRL		
Beryllium	0.0005	1	>90% of data below MRL		
Boron	0.1	10	0.06	0.08	0.11
Cadmium	0.001	0	>90% of data below MRL		
Chromium	0.01	6	0.001	0.042	0.083
Copper	0.01	5	>90% of data below MRL		
Fluoride	0.20	44	0.83	1.23	1.62
Iron	0.1	5	>90% of data below MRL		
Lead	0.005	1	>90% of data below MRL		
Manganese	0.05	1	>90% of data below MRL		
Mercury	0.0005	0	>90% of data below MRL		
Nickel	0.1	4	>90% of data below MRL		
Selenium	0.005	5	>90% of data below MRL		
Silver	0.001	2	>90% of data below MRL		
Thallium	0.005	0	>90% of data below MRL		
Zinc	0.05	22	0.07	0.11	0.15
Radiochemical Constituents					
Gross Alpha (piC/l)	Varies	42	2.3	13.3	24.3
Gross Beta (piC/l)	Varies	36	1.4	5.4	9.5
Ra-226 (piC/l)	Varies	1	>90% of data below MRL		
Ra-228 (piC/l)	Varies	1	>90% of data below MRL		
Uranium (Fg/l)	Varies	1	>90% of data below MRL		

All units mg/l except where noted with radiochemical constituents
Source [37]

The VOC, pesticide, and nitrogen isotope analytical results are provided in **Appendix B** and summarized below.

VOC Results - Analytical results of the VOC samples collected at 54 sites revealed detections at only one site. Bromodichloromethane, bromoform, chloroform, and dibromochloromethane, all organic disinfection byproducts of drinking water systems using free chlorine, were detected in the sample collected from a well in the Chiricahua Mountains.[34] No other VOCs on the EPA 502.2 VOC list or the EPA 8260B list, including the gasoline oxygenate, Methyl tertiary-Butyl Ether (MTBE), were detected at any sites. The analytes on the EPA 502.2 list are found in **Appendix C** and those on the EPA 8260B list are found in **Appendix D**.

Pesticide Results - Analytical results of the four samples collected for Groundwater Protection List (GWPL) analysis indicated that none of the pesticides were detected at any of the sites. **Appendix E** contains the MRLs of the pesticides on the GWPL.

Nitrogen Isotope Results - Nitrogen ($d^{15}N$) isotope samples were collected at seven sites where nitrate (as nitrogen) levels were > 7.5 mg/l in order to obtain additional information concerning potential nitrate sources. Analytical results ranged from 5.11 to 16.43 per mil. The $d^{15}N$ values typically range from +2 to +8 per mil for natural soil organic matter sources, -3 to +2 per mil for fertilizer sources, +6 - +25 per mil for septic wastewater systems, and +9 to +25 per mil for animal waste.[41] Thus, while nitrates at the site in the town of Dos Cabezas (16.43 mil) probably are due to septic systems, the other six samples which vary from 5.1 to 10.5 per mil are inconclusive and may result from a mixture of sources.

GROUNDWATER COMPOSITION

Groundwater in the WGB was characterized by qualitative classifications, chemistry, and cross-correlation of constituent concentrations.

General Summary - Groundwater in the WGB is generally *fresh*, *slightly alkaline*, and varies widely in hardness concentrations.

TDS concentrations (**Figure 8**) were considered *fresh* (below 1,000 mg/l) at 54 sites while 4 sites were *slightly saline* (1,000 to 3,000 mg/l).[23] Levels of pH were *slightly alkaline* (above 7 SU) at 53 sites and *slightly acidic* (below 7 SU) at 5 sites.[23]

Hardness concentrations (**Figure 9**) were divided into *soft* (13 sites), *moderately hard* (18 sites), *hard* (15 sites), and *very hard* (12 sites).[17] Most sample sites in the northern and southern portions of the basin exhibited a *calcium-bicarbonate* chemistry. Near the playa, sodium was often the dominant cation. A cluster of *calcium-sulfate* sites occurred near the Sulphur Hills (**Figure 8**).

Nutrient concentrations were generally low with only nitrate (**Figure 10**) and TKN detected at more than 10 percent of the sites. Nitrate (as nitrogen) concentrations were divided into *natural background* (10 sites at < 0.2 mg/l), *may or may not indicate human influence* (34 sites between 0.2 - 3.0 mg.l), *may result from human activities* (9 sites between 3.0 - 10 mg/l), and *probably result from human activities* (5 sites > 10 mg/l).[31]

Most trace elements such as antimony, arsenic, barium, beryllium, cadmium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and thallium were rarely detected. Only boron, chromium, fluoride (**Figure 9**), and zinc were detected at more than 10 percent of the sites.

Groundwater Chemistry - The chemical composition of sampled sites is illustrated using Piper trilinear diagrams (**Figure 11**):

- The cation triangle diagram (lower left in **Figure 11**) shows that the dominant (> 50 percent) cation is calcium at 32 sites, sodium at 15 sites, magnesium at 0 sites, and is mixed at 11 sites,

- The anion triangle diagram (lower right in **Figure 11**) shows that the dominant anion (> 50 percent) is bicarbonate at 47 sites, sulfate at 4 sites, chloride at 0 sites, and is mixed at 9 sites, and

- The cation-anion diamond diagram (in center of **Figure 11**) shows that the groundwater chemistry is *calcium-bicarbonate* at 32 sites, *sodium-bicarbonate* at 13 sites, *calcium-sulfate* at 10 sites, and *sodium-sulfate* at 3 sites.

Figure 8 - Groundwater Chemistry and TDS Levels in the Willcox Basin

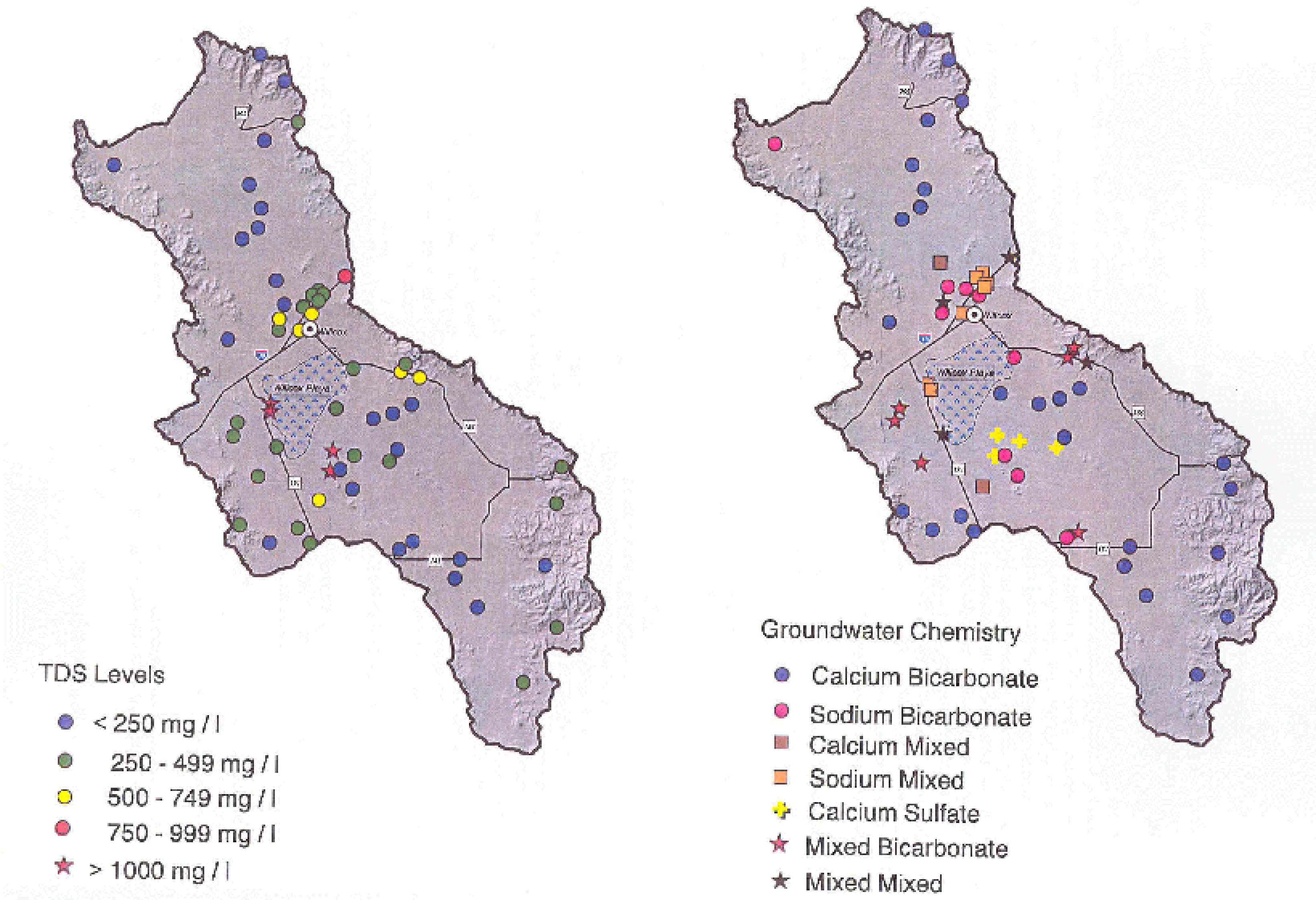


Figure 9 - Hardness and Fluoride Levels in the Willcox Basin

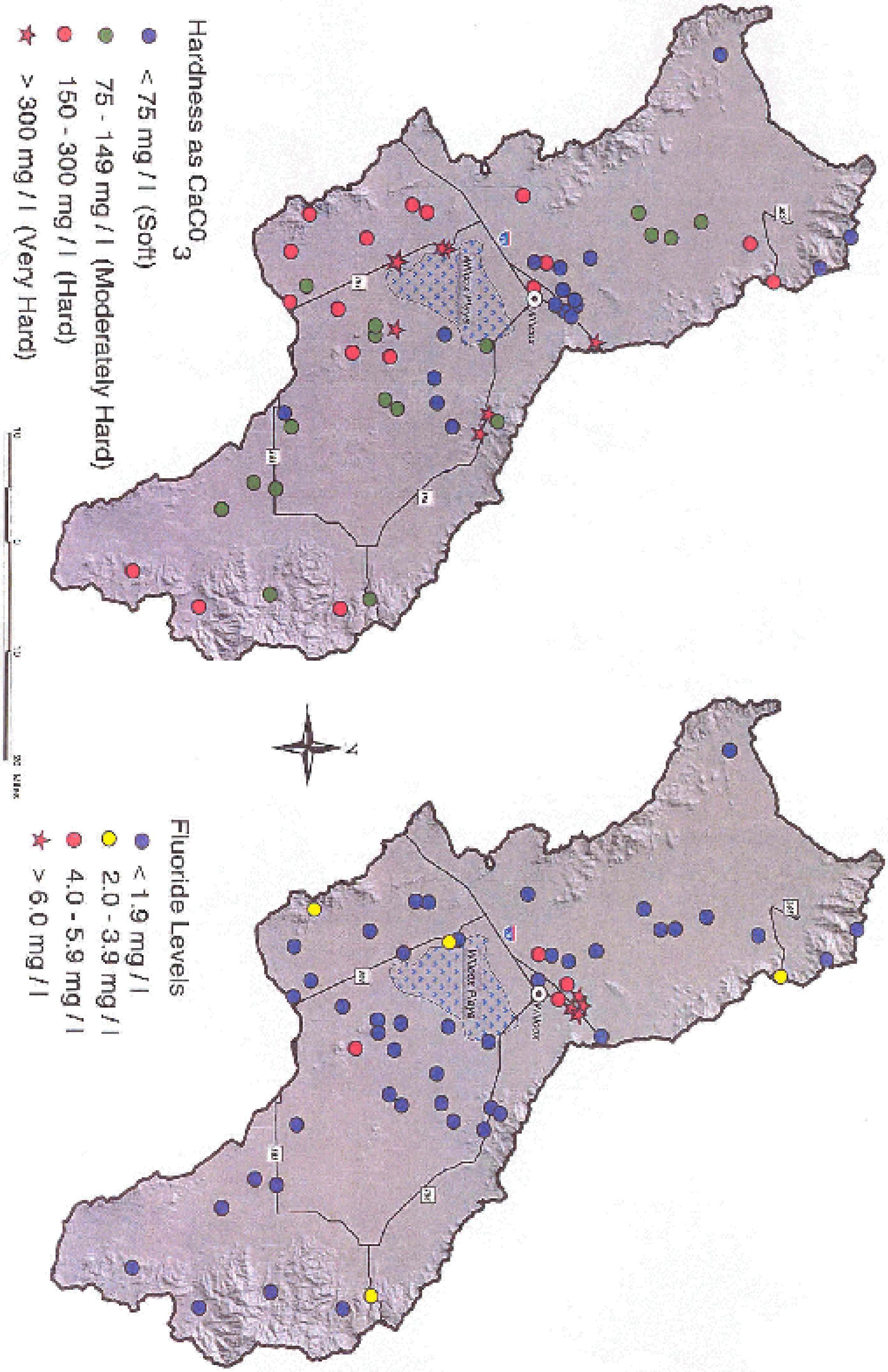
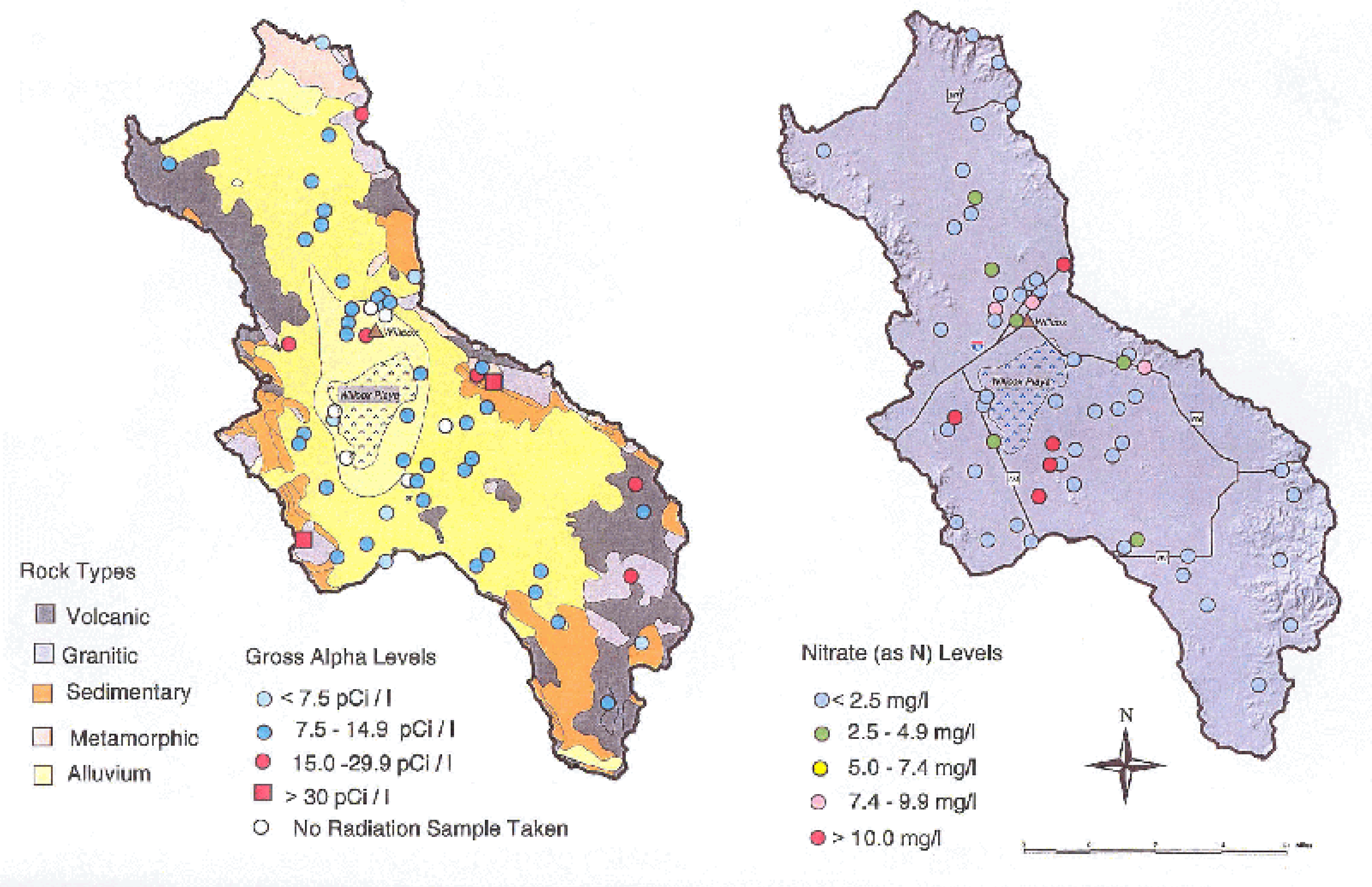


Figure 10 - Willcox Basin Rock Types, Gross Alpha and Nitrate Levels



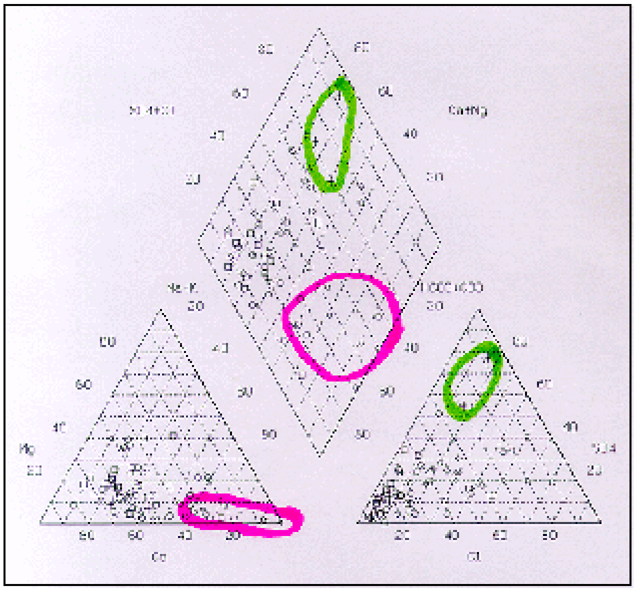


Figure 11. Sample sites plotted on a Piper tri-linear water chemistry diagram. Of particular interest are *calcium-sulfate* sites found in shallow wells in the Kansas Settlement District (highlighted in green) and *sodium-bicarbonate* sites found near the Spike E Hills (highlighted in pink). Sites in the northern part of the basin are symbolized by squares, sites in the southern WGB by circles.

The 58 groundwater sites were divided into three geological groups for chemical comparison: *hardrock*, *old alluvium*, and *young alluvium*. Empirical patterns appeared with each group: sites in *hardrock* and *old alluvium* were generally *calcium-bicarbonate* while sites in *young alluvium* were generally *sodium-bicarbonate* or *calcium-sulfate*.

Constituent Covariation - The covariation of constituent concentrations from random sites were determined to scrutinize the strength of the association. The results of each combination of constituents were examined for statistically-significant, positive or negative correlations. A ***positive correlation*** occurs when, as the level of a constituent increases or decreases, the concentration of another constituent also correspondingly increases or decreases. A ***negative correlation*** occurs when, as the concentration of a constituent increases, the concentration of another constituent decreases, and vice-versa. A positive correlation indicates a direct relationship between constituent concentrations; a negative correlation indicates an inverse relationship.

Many significant correlations occurred among the 46 random WGB sites. Generally, major ions as well as TDS were positively correlated. Four unique patterns emerged, many involving constituents with Primary MCL exceedances (Pearson Correlation Coefficient test, p# 0.05):

< pH was negatively correlated with calcium (**Figure 12**), magnesium, and bicarbonate (**Figure 13**).

< Gross alpha was positively correlated with TDS, calcium, sodium, bicarbonate, and chloride.

< Fluoride was positively correlated with both sodium and boron.

< Nitrate was positively correlated with TDS, chloride, calcium, magnesium, and hardness.

Twenty-nine (29) *alluvial aquifer* sites, a subset of the 46 WGB random sites, were analyzed for aquifer-specific significant patterns. Major ions, TDS, hardness, and boron were generally positively correlated. Four patterns emerged among the alluvial sites (Pearson Correlation Coefficient test, p# 0.05):

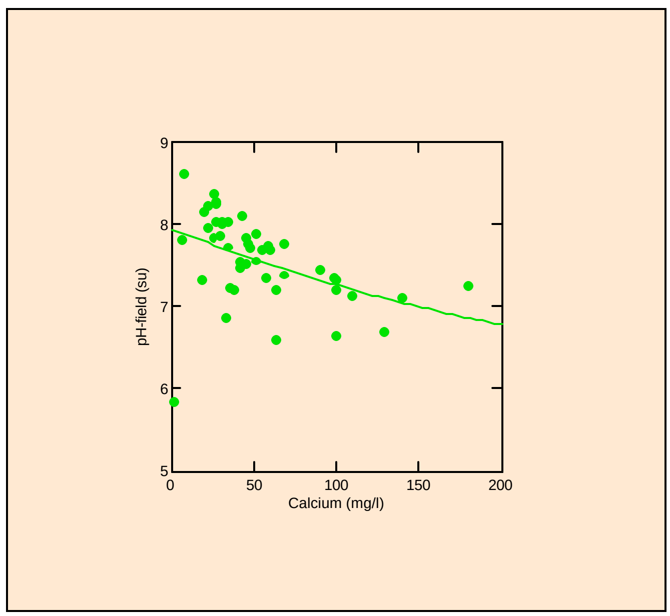


Figure 12. Calcium and pH have a negative correlation (Pearson Correlation Coefficient, p # 0.05). In a chemically-*closed hydrologic system*, calcium is removed from solution by precipitation of calcium carbonate and formation of smectite clays, while pH typically increases downgradient through silicate hydrolysis reactions.[38]

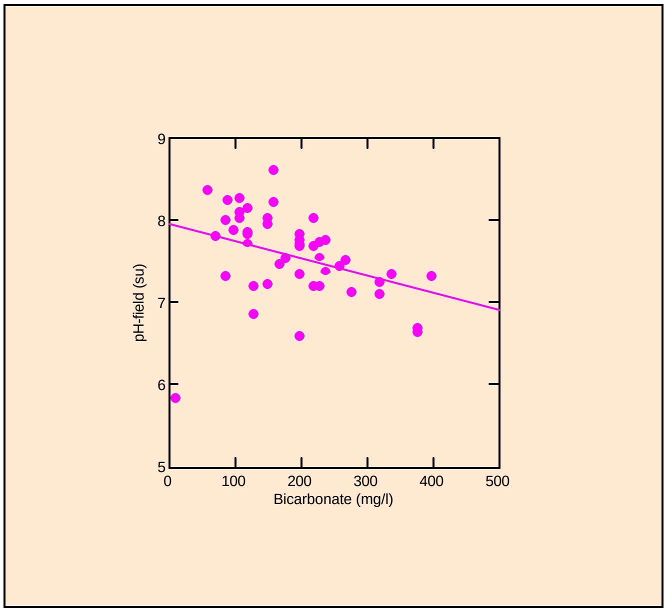


Figure 13. Bicarbonate and pH have a negative correlation (Pearson Correlation Coefficient, p # 0.05). In a *closed hydrologic system,* bicarbonate decreases as pH rises.[38]

< Fluoride was positively correlated with pH, sodium, and boron.

< Gross alpha and gross beta were positively correlated with temperature, TDS, and most major ions.

< pH was negatively correlated with calcium, gross alpha, gross beta, magnesium, hardness, and bicarbonate.

Seventeen (17) *hardrock* sites, a subset of the 46 WGB random sites, were analyzed for aquifer-specific significant patterns. Major ions as well as TDS, hardness, and boron were generally positively correlated. Three unique, significant patterns emerged among the *hardrock* sites (Pearson Correlation Coefficient test, p# 0.05):

< Gross alpha and gross beta were positively correlated only with sodium.

< Temperature was positively correlated with potassium and zinc.

< Five indicators of septic system impacts were all positively correlated: nitrate, chloride, TDS, TKN, and boron.[9]

GROUNDWATER QUALITY PATTERNS

Groundwater in the WGB was characterized by assessing the spatial variation of groundwater quality among aquifers, geologic classifications, and different portions of the basin. In addition, the vertical variation of groundwater quality in relation to groundwater depth was examined. These comparisons were conducted using groundwater quality data collected from 46 random sites.

Aquifer Comparison - The WGB is composed of the *alluvial aquifer*, the principal water-bearing unit comprising the valley floor, and *hardrock areas*, a limited water-bearing unit in the mountains surrounding the basin.[35]

Analytical results were compared between these two water-bearing units to examine for significant differences in concentrations of groundwater quality constituents. Four water quality constitutents, nitrate, pH (**Figure 14**), potassium, and temperature, were significantly higher in the *alluvial aquifer* compared to the *hardrock areas* (Kruskal-Wallis test, p # 0.05).

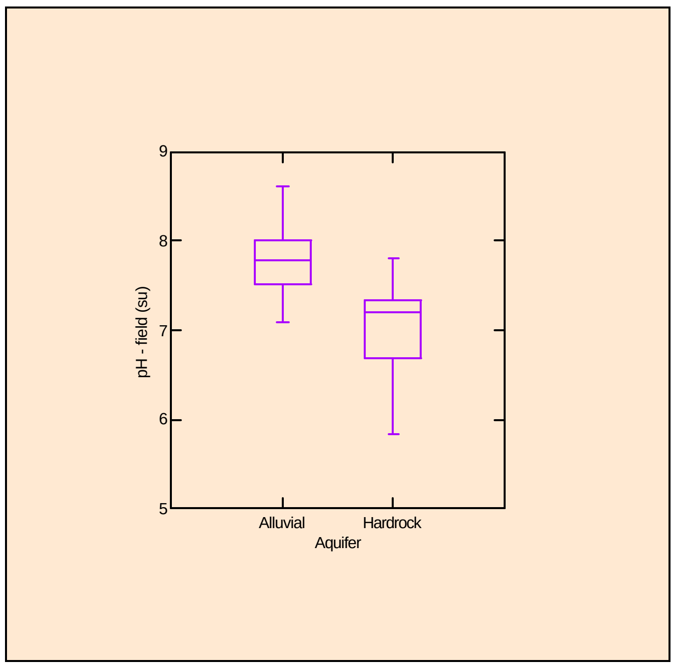


Figure 14. Levels of pH are significantly higher in the alluvial aquifer than in hardrock areas (Kruskal-Wallis test, p # 0.05). In hardrock areas, acidic precipitation averaging 5.8 su percolates into the ground. This recharged groundwater gradually increases in pH downgradient through silicate hydrolysis reactions.[38]

Geological Comparison - The WGB can be divided into six geologic classifications (**Figure 10**):

< **Young Alluvium** - composes the valley floor in proximity to the Willcox Playa.

< **Older Alluvium** - composes the valley floor in areas away from the Willcox Playa.

< **Granitic, Metamorphic, Sedimentary, and Volcanic Rocks** - are interspersed throughout mountainous areas of the basin.[5]

Analytical results were again examined for differences in concentrations of groundwater quality constituents among the six geologic classifications. Many significant patterns were revealed with this geological comparison (Kruskal-Wallis test, p# 0.05):

< Temperature was higher in *old alluvium* than in *metamorphic rock*.

< pH levels were higher in *old* and *young alluvium* than in *metamorphic* and *volcanic rock*.

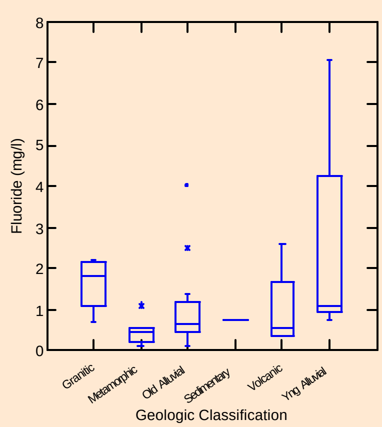


Figure 15. Fluoride concentrations are significantly higher in young alluvium than in old alluvium and metamorphic rock (Kruskal-Wallis test, p # 0.05). The young alluvium is found around the Willcox Playa, where the chemical groundwater evolution favors higher fluoride concentrations.

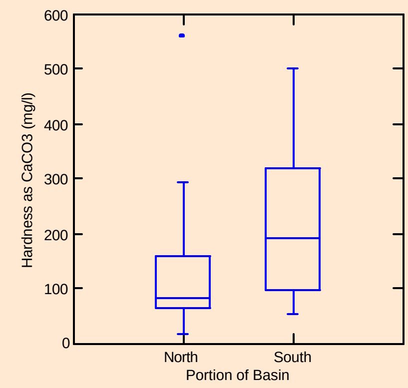


Figure 16. Hardness levels are significantly higher in the southern portion of the WGB than the northern part (Kruskal-Wallis test, p# 0.05). This difference may be because of recharge along the southern flowpath allowing additional inputs of calcium. In contrast, the northern part appears to be a *closed hydrologic system* that has little additional recharge along the flowpath. This chemical environment favors depleted calcium concentrations.

< Sodium concentrations were higher in *young alluvium* than in *old alluvium*, *metamorphic rock*, and *volcanic rock*.

< Gross alpha concentrations were higher in *granitic rock* than in *old* and *young alluvium*, *metamorphic* and *volcanic rock* (**Figure 10**).

< Fluoride concentrations were higher in *young alluvium* than in *old alluvium* and *metamorphic rock* (**Figure 15**).

Geographic Comparison - The WGB was divided into several portions for further analyses:

< **Northern portion** - drains the area north of Willcox Playa including recharge from the Pinaleno Mountains.

< **Southern portion** - drains the area south of Willcox Playa including recharge from the Chiricahua Mountains.

Bicarbonate, calcium, hardness (**Figure 16**), sulfate, and total alkalinity had higher concentrations in the southern portion than the northern portion (Kruskal-Wallis test, p# 0.05).

Groundwater Depth Comparison - The vertical variation of groundwater quality was examined by comparing constituent concentrations with groundwater depth in the WGB. Constituent concentrations for the basin as a whole were compared to groundwater depth below land surface (bls) for correlations. Many constituent concentrations tended to significantly decrease with increasing groundwater depth bls. Bicarbonate, calcium, chloride (**Figure 17**), gross alpha, hardness, sodium, SC, sulfate, total alkalinity, TDS, and TKN followed this pattern. In contrast, pH-field, temperature (**Figure 18**), and zinc had concentrations that increased with increasing groundwater depth (regression analysis, p # 0.05).

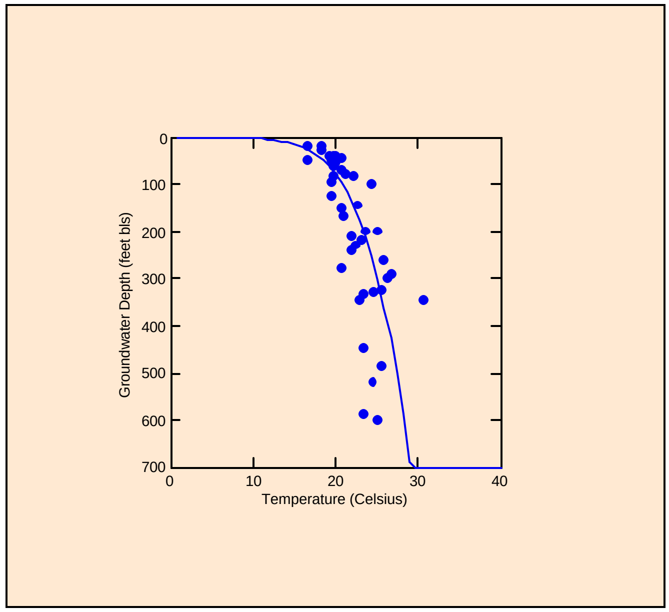


Figure 18. Temperatures generally increase with increasing groundwater depth bls (regression analysis, p # 0.05). Groundwater temperatures increase approximately 3 degrees Celsius with every 328 feet in depth.[10]

Constituent concentrations from *alluvial aquifer* sample sites were compared with groundwater depth for significant trends. Concentrations of bicarbonate, boron, chloride, fluoride, sodium, SC, sulfate, total alkalinity, and TDS decreased with increasing groundwater depth bls; in contrast, temperature levels increased with increasing groundwater depth bls (regression analysis, p # 0.05)

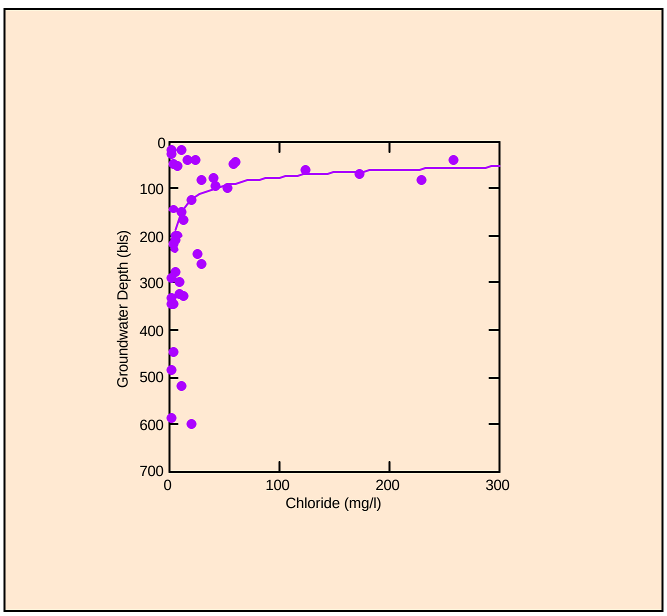


Figure 17. Chloride concentrations generally decrease with increasing groundwater depth bls (regression analysis, p # 0.05). These constituents, with the exception of TKN, show a pattern similar to chloride in which a *critical level* is attained at approximately 110 feet bls. Constituent levels remain generally constant at groundwater depths greater than the *critical level* and are highly variable and sometimes dramatically higher at more shallow depths.

Constituent concentrations from *hardrock areas* were compared with groundwater depth. Concentrations of potassium, pH, temperature, and zinc increased with increasing groundwater depth bls; in contrast, sulfate and TKN concentrations decreased with increasing groundwater depth bls (regression analysis, p # 0.05).

Groundwater Quality Time Trend Analysis

A limited time-trend analysis was conducted by comparing groundwater quality data collected from the same 5 sites approximately 10 years apart. The sites, sampled by ADWR between 1987 and 1991 were resampled by ADEQ for this study.[35] TDS, temperature, ph-field, SC-field, total alkalinity, hardness, bicarbonate, calcium, chloride, fluoride, magnesium, nitrate, potassium, sodium, sulfate, and zinc were examined for changes during these time periods. No significant changes in constituent concentrations were found (Wilcoxon test, p # 0.05).

CONCLUSIONS

Groundwater quality of the WGB was assessed in 1999 by the ADEQ Groundwater Monitoring Unit. Sampling was conducted at 58 sites: 46 randomly-selected and 12 targeted. Groundwater samples were collected for inorganic analyses at all sites, for VOCs and radiochemistry analyses at most sites, and for nitrogen isotope and GWPL pesticide analyses at a few sites.

The conclusions of this study are summarized in three different sections:

- Groundwater suitability for domestic use,
- Groundwater quality patterns unique to sub-areas of the basin, and
- Study design and data evaluation.

Suitability of Groundwater for Domestic Use

Thirty-six (36) percent of sites had at least one constituent exceeding a health-based, Primary MCL standard. ***Primary MCL exceedances were largely concentrated in three areas:***

- ***The Spike E Hills, northeast of the city of Willcox*** (arsenic and fluoride),
- ***Areas of granitic rock*** (gross alpha), and
- ***Northwest of the Sulphur Hills*** (nitrate and fluoride).

The four Primary MCL exceedances outside these areas (nitrate near the Red Bird Hills and the Circle I Hills, gross alpha near Willcox, and antimony near Kansas Settlement) appear to be localized in nature judging from nearby sample sites. The gross alpha exceedance near Willcox may be related to Tertiary-Quaternary lakebed deposits known to contain high uranium concentrations.[19]

Similarly, 40 percent of sites had at least one constituent exceeding an aesthetics-based, SDW Secondary MCL guideline. ***Secondary MCL exceedances were largely clustered in three areas:***

- ***Near the Spike E Hills, northeast of the town of Willcox*** (fluoride and pH),
- ***Northwest of the Sulphur Hills*** (sulfate), and.
- ***Immediately west of Willcox Playa*** (chloride and
- sulfate).

Other Secondary MCL exceedances occurred with fluoride at three widely-scattered *hardrock* sites, TDS at five sites near the Dos Cabezas Mountains and the Willcox Playa, iron at one site near the Sulphur Hills, and manganese at one site in the Chiricahua Mountains. These dispersed fluoride exceedances may be associated with volcanic rocks and their weathering products.[29] The iron and manganese exceedances appear to be site specific and may not reflect regional groundwater quality conditions.

Based upon comparing the results of this regional study with water quality standards/guidelines, ***groundwater in large expanses of the WGB, particularly in alluvial areas not in close proximity to the Willcox Playa and Sulphur Hills, appears to be largely suitable for domestic purposes.***

Groundwater Quality Patterns Unique to Sub-Areas of the Basin

Unique groundwater quality patterns or occurrences were examined in this study for the following aspects of the WGB:

- Northern portion above the Willcox Playa,
- Southern portion below the Willcox Playa,
- *Alluvial aquifer*, and
- *Hardrock areas.*

Northern Portion of the Willcox Basin

Three aspects of the northern portion of the WGB, known as the Stewart District, are further discussed in this section:

- Trace elements near the Spike E Hills,
- Groundwater evolution, and
- Low TDS concentrations.

Trace Elements near the Spike E Hills - Fluoride and arsenic concentrations exceeding health-based water quality standards were found 3.5 miles northeast of the city of Willcox. This impacted area is centered around a small hardrock outcrop, the Spike E Hills.

The six groundwater sample sites within 1.5 miles of the Spike E Hills all exceeded the 4.0 mg/l Primary MCL for fluoride, with concentrations reaching 10.0 mg/l. Three sites exceeded the 0.5 mg/l Primary MCL

for arsenic, with concentrations as high as 1.0 mg/l.
Four sites exceeded the 8.5 SU Secondary MCL for pH, with levels as high as 9.7 SU.

Previous studies have noted fluoride concentrations in this area, and around the Willcox Playa in general, that may be extremely high as a result of evaporative concentration.[29 39] Other fluoride sources in the area appear to be in the lake-bed deposits as well as the volcanic and older metamorphic rocks surrounding the basin.[6 29]

Figure 19. Elevated fluoride, arsenic, and pH levels are found near the Spike E Hills (tan-colored in the foreground), a small metamorphic rock outcrop approximately three miles northeast of the city of Willcox. Groundwater in the area was characteristically soft, alkaline, and of a sodium-mixed anion chemistry and may be the result of water upwelling from great depths from the nearby Apache Pass Fault.[20] The Winchester Mountains are seen in the background.

There appear to be several controls on fluoride at sites near the Spike E Hills:

- Availability of the fluoride ion in alluvium and/or rocks,
- Calcium concentrations, and
- Hydroxyl ion exchange.

Calcium is an important control of higher fluoride concentrations (> 5 mg/l) through precipitation of the mineral fluorite.[38] In a *chemically closed hydrologic system*, calcium is removed from solution by precipitation of calcium carbonate and formation of smectite clays.[39] High concentrations of dissolved fluoride may occur in groundwater depleted in calcium if a source of fluoride ions is available for dissolution.[39]

Results from this study support this finding. The four sites with fluoride concentrations greater than 7 mg/l had corresponding depleted calcium concentrations (< 9 mg/l) constituting less than 5 percent of the total cation amount. Each of the four sites also had a strongly alkaline pH (> 8.6 SU).

Exchange of sorption-desoprtion reactions appear to be the most important control for lower (< 5 mg/l) fluoride concentrations. In recharge areas, weathering of rocks releases fluoride ions into solution. The fluoride ions may be initially exchanged for hydroxyl groups on montmorillonitic clays, a process which is favored by near neutral pH conditions, the electronegativity of fluoride, and the identical size of the fluoride and hydroxyl ions.[39] As pH levels increase downgradient, greater levels of hydroxyl ions may affect an exchange of hydroxyl for fluoride ions, thereby increasing the fluoride in solution.[38]

Arsenic concentrations may be influenced by similar reactions including exchange on clays or oxyhydroxides. Oxidizing waters allow arsenic to be converted to their more soluble oxyanion form in their highest oxidation state.[40] Other factors such as aquifer residence time, lithology, and clay mineralogy could also be important factors influencing arsenic concentrations.

The sites near the Spike E Hills had a *sodium-mixed anion* chemistry, with very low concentrations of calcium and magnesium. Groundwater chemistry in the WGB is predominately *calcium-bicarbonate*; the high sodium levels found in the Spike E Hills area may be due to several reasons including silicate weathering and halite dissolution.[40] Cation exchange of calcium and magnesium in the water for sodium adsorbed on clays has also been suggested as an important process.[43] Other sources indicate that in dilute waters, ion exchange accounts for little, if any, solute sodium, the major ion replaced on the substrate, although these dilute waters are sodic in composition.[40] The slightly elevated bicarbonate concentrations in the area can occur in some groundwater that is low in calcium and magnesium, especially where processes releasing carbon dioxide are occurring within the aquifer.[27]

Similar cases of *soft*, sodium-dominated groundwater occurring with high pH levels and elevated concentrations of trace elements such as fluoride, arsenic, and boron have been found in other Arizona basins.[15 46] The correlation of arsenic and fluoride concentrations was also noted in Southwestern basins.[40] These correlations suggest a relationship between processes controlling the concentrations of these constituents.

Geology may be the reason these processes are occuring near the Spike E Hills. This hardrock formation is composed of quartzite of the pinal schist, a metamorphic rock.[20] The Apache Pass fault runs just to the north of the Spike E Hills separating their quartzites from the metasediments and metavolcanics of the Circle I Hills.[20] While the groundwater quality effects of the Apache Pass fault are unknown, other studies in nearby basins have found higher constituent levels close to major faults.[16] Fault zones may produce water from great depths that often has a sodium-dominated chemistry.

Groundwater Evolution - Groundwater in the valley alluvium of the Stewart District is typically a *calcium-bicarbonate* type until evolving into a *sodium-mixed anion* chemistry near the playa, a pattern found by previous studies.[35 40] This groundwater chemistry pattern is typical of a *closed hydrologic system* in which the aqueous chemistry is determined solely by the reactions of the initial recharge water with the various minerals as it moves downgradient.[40]

This *chemically closed hydrologic system* assessment is supported by generally decreasing concentrations of bicarbonate and calcium as well as increasing concentrations of sodium, sulfate, chloride, and pH along a flowpath stretching from Mt. Graham (**Figure 20**) to the Willcox Playa. Recharge areas typically have a *calcium-bicarbonate* chemistry[40] with the bicarbonate acquired though dissolution of soil-zone carbon dioxide by percolating precipitation as well as from evapotranspirative concentration of dissolved constituents in the precipitation.[43] The evaporite deposits near the Willcox Playa are a natural water softener, transforming groundwater chemistry into one dominated by sodium cations. An anomaly occurs when this pattern reverses itself near the playa with groundwater sample WCX-30/31. This may indicate some recharge is occurring away from the mountain fronts.

Low TDS Concentrations - Groundwater in the Stewart District is noteworthy for its low TDS concentrations. Several factors may influence low TDS concentrations including low rock solubility, a poor supply of carbon dioxide species, and the lack of significant impacts from human activities.[26] This dilute water influences economic activities such as the recent construction of many greenhouse operations in this area. The source of much of this groundwater is recharge from the Pinaleno Mountains, one of the two principal recharge areas in the basin.[25]

This TDS trend begins at sites in the most upgradient areas atop Mt. Graham in the Pinaleno Mountains. The two springs sampled (**Figure 21**), WCX-36 and WCX-37, had very low respective TD concentrations of 78 mg/l and 46 mg/l. The most upgradient spring,

Figure 20. Covered by clouds, Mt. Graham rises abruptly from the valley floor alluvium. This northern part of the WGB appears to be a *closed hydrologic system* in which the aqueous chemistry is determined solely by the reactions of the initial recharge water with the various minerals as it moves downgradient.[40]

appears to consist of almost unadulterated rainfall with a pH of 5.83 SU which is near the frequently observed pH of precipitation.[27] This spring discharge may be controlled by a fault or fracture system, providing a direct route from recharge to discharge, and diminishing residence and reaction times.[40] The low TDS concentrations, typically below 200 mg/l, continue into the central portion of the Stewart District almost as far south as the Willcox Playa. Near the playa, evaporation and transpiration of groundwater along with evaporation of surface water has deposited soluble material that results in increasingly mineralized groundwater.[25]

Figure 21. The lush, verdant vegetation found atop Mt. Graham at Treasure Park Spring (WCX-36) contrasts with the typically dry conditions found near the Willcox Playa. Groundwater is very dilute in the Pinaleno Mountains and these low TDS levels continue southward through the Stewart District.

These low, Stewart District TDS concentrations are also reflected in significantly lower bicarbonate, calcium, hardness, and sulfate concentrations in the northern portion of the basin (Kruskal-Wallis test, p # 0.05).

The differences in constituent concentrations between the northern and southern portions of the WGB may also be related to wells in the Kansas Settlement area producing water from both the consolidated and unconsolidated alluvium. In contrast, wells in the Stewart District produce water from only the unconsolidated alluvium as the consolidated alluvium consists of fine-grained material that yields little or no water to wells.[11] Previous studies have also noted that many wells in this area, due to the poor condition of the well casings and to shallow perforation intervals, act as conduits by which irrigation tail water cascades down the wellbores and blends with the water in the regional aquifer.[35] This cascading water does not seem to have affected groundwater quality to the degree it has in the Kansas Settlement area.

Southern Portion of the Willcox Basin

Three aspects of groundwater quality in the southern portion of the WGB are discussed in this section:

- Fluoride near the Sulphur Hills,
- Elevated constituents near Kansas Settlement, and
- Groundwater evolution.

Fluoride near the Sulphur Hills - Near the Sulphur Hills, fluoride concentrations exceed the Primary MCL at one site and Secondary MCLs at two sites. These sites represent the southern extension of a band of high fluoride concentrations stretching from north of the Willcox Playa to the Sulphur Hills.[32] Fluoride concentrations near the Sulphur Hills are thought to be associated with rhyolitic volcanic geology, nearby volcanic flows, and the weathering products of these rocks.[29 39]

Elevated constituents near Kansas Settlement - Groundwater of very different compositions were collected from shallow and deep wells near the farming community of Kansas Settlement. Additional sites were subsequently sampled in this area to delineate constituent concentration differences with groundwater depth. Wells were divided into these two qualitative categories based on whether their groundwater depths were less than or greater than the *critical groundwater level* (about 110 feet bls).

In comparing six deep samples and seven shallow sites in the area, levels of TDS, calcium, magnesium, hardness, sodium, and chloride were significantly higher in the shallow samples; in contrast, temperature levels were significantly higher in the deeper samples (Kruskal-Wallis test, p # 0.05). Primary MCL exceedances occurred at three shallow sites for nitrate and at one shallow site apiece for antimony and fluoride. Secondary MCL exceedances occurred at three shallow sites for TDS, at two shallow sites for sulfate, and at one shallow site for iron. Antimony and iron were otherwise rarely detected in the basin. These exceedances and patterns may be partially due to land uses in the area.

The Kansas Settlement is an area of intensely farmed lands and it seems probable that the shallow sites may have been impacted by groundwater recharge from irrigation applications. Excess water from irrigation applications may recharge the aquifer, especially in locations where groundwater depth is less than 100 feet bls.[29,35] This recharge may be contributing to the higher salinity found in the shallow wells. Nitrate isotope samples collected in this area were inconclusive but may indicate that other sources of nitrate, such as septic systems, may also be impacting shallow groundwater.

Deterioration of groundwater quality associated with irrigation development has been observed worldwide including other agricultural areas of Arizona.[26,45] Using tritium isotopes, recent and historic agricultural recharge to groundwater was identified in the Upper Santa Cruz basin and found to be higher in some constituents including TDS and calcium.[16] A major source of calcium in agricultural areas is calcite, which tends to become concentrated in soils by evaporation. During irrigation, the calcite is dissolved by the water which percolates to the aquifer.[16] In Gila Valley within the Yuma basin, many major ions were found to be significantly higher than in other portions of the basin.[45] Recycling of groundwater was also thought to be the source of the elevated constituents.[45] Concentrations of nitrate and pesticides in this deep percolation recharge water can be reduced by utilizing best management practices, but salt loadings on the groundwater cannot be reduced at this time.[13]

Groundwater Evolution - Examining a flowpath along the course of Turkey Creek, groundwater in the upgradient areas in the Chiricahua Mountains and nearby valley alluvium is typically *calcium-bicarbonate* until evolving into *sodium-bicarbonate* near the Sulphur Hills, and finally into *calcium-sulfate* near the playa. This groundwater chemistry pattern is supported by previous studies.[35,40]

Although an earlier study indicated little or no recharge resulting from direct precipitation from the valley floor,[11] the WGB had been previously classified as an *open hydrologic system*.[40] This is one in which groundwater chemistry is in part controlled or influenced by atmospheric gases or liquids that enter the system along flow paths subsequent to initial recharge.[40] This determination was based upon increases in concentrations of bicarbonate and calcium and decreases in sodium, sulfate, chloride, and pH at points along a flow path stretching along Turkey Creek from the Chiricahua Mountains to the Willcox Playa. High precipitation levels, relatively shallow groundwater levels, and the lack of a clay confining layer overlaying the aquifer are thought to be factors enabling the mixing of additional recharge water in valley areas with underflow from the mountain front recharge areas.[40]

Similar to previous studies, data from this ADEQ study also showed increases in levels of bicarbonate and calcium and decreases in levels of sodium, sulfate, chloride, and pH at points along the Turkey Creek flow path which supports the *open hydrologic system* assertion.

Alluvial Aquifer

In the WGB, most drainage is interior and flows to the Willcox Playa. Basins having interior drainage from which solutes cannot escape often have high groundwater TDS concentrations owing to evaporation of water and the continued influx of solutes.[26] In the WGB, TDS concentrations exceeding 1,000 mg/l were found in a narrow area surrounding the playa, a pattern also mirrored by prior studies.[32]

This interior drainage pattern influences chloride and sodium concentrations that are significantly higher at sites nearer the playa in the *younger alluvium* than toward the uplands in the *old alluvium* (Kruskal-Wallis test, p # 0.05). Sites west of the playa near the town of Cochise seem particularly effected. As the only *sodium-chloride* sites in the WGB, they exceeded Secondary MCLs for chloride, fluoride, sulfate, and TDS. Dissolution of evaporative salts was cited as the most probable source of increasing chloride and sodium levels near playa areas.[43] Sodium, chloride, and sulfate form the most soluble salts in desert soils and would be easily dissolved by water flushing through the unsaturated zone.[43]

Hardrock Aquifer

Of the 13 sample sites in *hardrock*, six exceeded the 15 piC/l Primary MCL for gross alpha. These exceedances occurred near areas of *granite rock* in the Chiricahua, Dos Cabezas, Dragoon, and Pinaleno Mountains. Gross alpha exhibited a pattern where levels were significantly higher at sites in *granite rock* than in either *old* and *young alluvium* (Kruskal-Wallis test, p # 0.05). The highest gross alpha concentrations were found near Cochise Stronghold in the Dragoon Mountains (62 piC/l) and in the historic mining community of Dos Cabezas (239 piC/l). The latter site also exceeded the 5.0 piC/l Primary MCL for radium-226+228 with a level of 27.2 piC/l

Radiochemistry levels are typically elevated in areas of *granite rocks*.[29] As in other Arizona groundwater basins, the highest gross alpha and radium-226+228 concentrations were found in areas of *granite rock* where mining activity had occurred nearby, such as near the community of Chloride in northwest part of the state.[47] A probable explanation for this phenomena is the increased rock surface exposure because of the mining.

Study Design and Data Evaluation

Methods of Investigation - Groundwater sample sites were selected using two strategies. A systematic, grid-based, random site-selection approach was used to investigate the regional groundwater quality; 46 sites were selected using this method. Twelve (12) sites were targeted in areas where additional groundwater quality information was thought to be valuable to the study. The sample collection methods for this study conformed to the *Quality Assurance Project Plan*[2] and the *Field Manual for Water Quality Sampling*.[7]

Data Evaluation - Quality assurance procedures were followed and quality control samples were collected to ensure the validity of the groundwater quality data. Analysis of equipment blank samples indicated systematic contamination of SC-lab and turbidity; however, the extent of the contamination by these parameters was not considered significant. Analysis of duplicate and split samples revealed excellent correlations; only turbidity and TKN analyses had wide median differences of 33 percent and 15 percent, respectively. Data validation was also examined in six QA/QC correlations that affirmed the acceptability of the groundwater quality data for further analysis. Overall, the effects of sampling procedures and laboratory methods on the samples were not considered significant.

Data analysis for this study was conducted using Systat software.[49] The non-normality of both the non-transformed data and the log-transformed data was determined by using the Kolmogorov-Smirnov one-sample test with the Lilliefors option.[12] Spatial variations in constituent concentrations were investigated using the non-parametric Kruskal-Wallis test.[24] Vertical or groundwater depth variations were examined using three regression models. Correlations among constituent concentrations were analyzed using the Pearson Correlation Coefficient test.[24] Constituent concentration changes over time wer test.[24] e investigated using the Wilcoxon rank-sum Determining *critical levels* of groundwater depth bls for constituent concentrations used the Cate-Nelson method.[42]

RECOMMENDATIONS

Recommendations for domestic well owners, public water supply systems, and future groundwater quality studies are provided in this section. These are based on interpretations of the analytical results from groundwater samples collected for this study.

The following recommendations are provided for domestic well owners in the WGB.

- ADEQ encourages well owners concerned about their water supply to periodically collect samples, with the assistance of certified laboratories, for analysis of the full range of groundwater quality constituents. The ADHS, Environmental Laboratory Licensure and Certification Section at (602) 255-3454 provides a list of certified labs.

- Well owners interested in less expensive and more targeted testing of their water source should include in their sampling and analysis the following constituents: fluoride and arsenic near the Spike E Hills, nitrate near Kansas Settlement, fluoride near the Sulphur Hills, and gross alpha near *granite rock*, especially around Dos Cabezas. Primary MCL exceedances may exist in other areas of the WGB; however, based upon the results of this regional groundwater quality report, their occurrence should not be widespread in nature. Again, it should be noted for full assurance that groundwater pumped by a private well meets all water quality standards for domestic use, tests should be conducted on a wide range of groundwater quality constituents.

- ADEQ encourages well owners to inspect and, if necessary, repair faulty surface seals, degraded casing, or other factors that may affect well integrity. Septic systems should also be inspected periodically to assure safety and compliance with ADEQ's *Engineering Bulletin #12*.[1]

The following recommendations are provided for public water systems within the WGB.

- Groundwater quality data collected during this study should assist in the site selection process of new public supply wells. Some sample sites exceeded health-based, water quality standards and caution should be used in these areas when developing new public water supplies.

The following recommendations are provided for future groundwater quality studies within the WGB.

- Resampling of the ADEQ index wells appears to be unnecessary at intervals of less than approximately ten years. The time-trend analysis indicates that constituent concentrations did not significantly change between 1990 and 1999 (Willcoxon test, p#0.05). This suggests that most of the constituents are largely controlled by natural factors and are not prone to vary significantly over time in the near term.

- Individual flow paths could be examined to better understand the specific geochemical reactions occurring within the study area.

- Tritium isotope samples could be collected in the Kansas Settlement area to better understand sources of the elevated constituent concentrations found in shallow groundwater in the area.

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Appendix A. Data on Sample Sites, Willcox Basin, 1999

Sample #	Cadastral	Latitude - Longitude	ADWR #	ADEQ #	Sample Type	Well Depth	Water Depth	Aquifer	Geology
		1st Field Trip, May 24 - 27, 1999 - Towne & Freark (Equipment Blank WCX-07)							
WCX-01/02	(D-13-25)21bbb	32°17'42.617" 109°48'24.334"	646654	57854	Random	162'	84'	Alluvial	Young alluvium
WCX-03	(D-14-26)25dbc	32°11'08.408" 109°38'38.739"	630550	49716	Random	225'	80'	Hardrock	Sedimentary
WCX-04	(D-14-27)19ccc	32°11'51.565" 109°37'58.268"	spring	38111	Random	spring	spring	Hardrock	Metamorphic
WCX-05	(D-12-23)12cca	32°24'10.117" 109°57'33.820"	519033	57855	Random	300'	170'	Alluvial	Old alluvium
WCX-06	(D-12-24)05bbc	32°25'14.254" 109°55'28.427"	646152	57856	Random	300'	150'	Alluvial	Old alluvium
WCX-08	(D-13-24)03bcd	32°20'00.282" 109°53'19.279"	557335	57856	Random	230'	125'	Alluvial	Old alluvium
WCX-09	(D-15-24)21abb	32°07'17.047" 109°54'22.509"	505008	57858	Random	100'	40'	Alluvial	Young alluvium
WCX-10	(D-15-26)28bbd	32°06'26.206" 109°42'10.179"	612120	57859	Random	500'	200'	Alluvial shallow	Old alluvium
WCX-11	(D-15-25)23bba	32°07'22.462" 109°46'15.198"	none	57860	Random	100'	50'	Alluvial	Young alluvium
WCX-12	(D-16-25)23cdd	32°01'23.115" 109°46'15.786"	617501	39827	Random	235'	97'	Alluvial shallow	Old alluvium
WCX-13	(D-16-25)23cdd	32°01'21.156" 109°46'19.124"	617503	57851	Random	480'	175'	Alluvial deep	Old alluvium
WCX-14	(D-14-23)10aab	32°14'14.748" 109°59'15.382"	514874	57853	Random	401	345'	Alluvial	Old alluvium
WCX-15	(D-14-24)03abb	32°15'09.717" 109°52'58.646"	522506	57847	Random	90'	53'	Alluvial	Young alluvium
WCX-16	(D-14-24)01abd	32°15'05.746" 109°50'35.030"	648317	57848	Random	85'	45'	Alluvial	Young alluvium
WCX-17/18	(D-14-27)32bdd	32°10'24.768" 109°36'47.539"	500741	57849	Random	300'	70'	Hardrock	Granitic
WCX-19	(D-14-25)25cdc	32°10'57.048" 109°45'12.331"	644456	57850	Random	100'	42'	Alluvial	Young alluvium
WCX-20	(D-15-26)23cdd	32°06'31.046" 109°39'43.486"	611564? 611586?	39117	Random	760'	370'	Alluvial deep	Old alluvium
		2nd Field Trip, June 16-18, 1999 - Towne & Freark (Equipment Blank WCX-24)							
WCX-21	(D-15-27)18aca	32°07'56.414" 109°37'31.643"	517239	57829	Random	750'	600'	Alluvial	Old alluvium
WCX-22	(D-16-26)18acc	32°02'38.459" 109°44'12.445"	528271	57830	Random	400'	200'	Alluvial shallow	Old alluvium
WCX-23	(D-18-26)01bbb	31°53'31.200" 109°39'01.726"	632699	57831	Random	331'	145'	Alluvial	Old alluvium

Appendix A. Data on Sample Sites, Willcox Basin, 1999--Continued

Sample #	Cadastral	Latitude - Longitude	ADWR #	ADEQ #	Sample Type	Well Depth	Water Depth	Aquifer	Geology
WCX-25/26	(D-16-27)07dcc	32°03'13.110" 109°39'17.282"	627054	39939	Random	650'	290'	Alluvial	Old alluvium
WCX-27	(D-17-26)06bbb	31°59'26.277" 109°44'38.571"	553932	57832	Random	350'	230'	Alluvial	Old alluvium
WCX-28	(D-17-25)09bcc	31°58'15.293" 109°48'45.779"	800060	57833	Random	400'	100'	Alluvial	Old alluvium
WCX-29	(D-18-27)25aaa	31°50'46.868" 109°32'30.160"	617994	41463	Random	390'	220'	Alluvial	Old alluvium
WCX-30/31	(D-13-24)27dca	32°16'12.937" 109°52'54.295"	627208	57834	Random	87'	61'	Alluvial	Young alluvium
3rd Field Trip, August 10-12, 1999 - Towne & Freark (Equipment Blank WCX-40)									
WCX-32	(D-16-25)10dda	32°03'16.136" 109°46'46.073"	650713	58010	Random	125'	N/A	Alluvial shallow	Young alluvium
WCX-33	(D-13-25)17bbd	32°18'36.370" 109°49'23.745"	649019	58011	Targeted	150'	95'	Alluvial	Young alluvium
WCX-34	(D-13-24)23bcc	32°17'23.473" 109°52'27.147"	546887	58012	Targeted	102'	69'	Alluvial	Young alluvium
WCX-35	(D-10-24)01aaa	32°35'43.440" 109°50'58.042"	spring	58013	Random	spring	spring	Hardrock	Granitic
WCX-36	(D-9-24)10	32°39'45.165" 109°52'13.813"	spring	58014	Random	spring	spring	Hardrock	Metamorphic
WCX-37	(D08-24)29cbb	32°42'27" 109°55'8"	spring	58021	Random	spring	spring	Hardrock	Metamorphic
WCX-38/39	(D-16-29)26dad	32°00'38.781" 109°21'18.196"	629082	58015	Random	116'	28'	Hardrock	Volcanic
WCX-41	(D-16-26)23baa	32°02'09.079" 109°40'10.592"	622696	58016	Random	1018'	326'	Alluvial deep	Old alluvium
4th Field Trip, September September 22-24, 1999 - Towne & Freark (Equipment Blank WCX-51)									
WCX-42	(D-18-28)07dca	31°52'40.601" 109°31'53.720"	536861	58000	Random	446'	335'	Alluvial	Old alluvium
WCX-43	(D-19-28)08aba	31°47'57.321" 109°30'03.465"	649320	41944	Random	550'	486'	Alluvial	Old alluvium
WCX-44/45	(D-13-25)21bbb	32°17'48.600" 109°48'20.196"	648188	58001	Targeted	160'	115'	Alluvial	Young alluvium
WCX-46	(D-18-27)06aad	31°54'06.285" 109°37'43.011"	618491	58002	Random	350'	280'	Alluvial	Old alluvium
WCX-47	(D-17-24)25daa	31°55'32.879" 109°50'59.162"	519310	58003	Random	450'	330'	Alluvial	Old alluvium
WCX-48	(D-15-23)26ddd	32°05'57.051" 109°57'46.519"	605724	58004	Random	590	260	Alluvial	Old alluvium
WCX-49	(D-16-23)02aab	32°04'43.665" 109°58'27.770"	605726	58005	Random	426	200	Alluvial	Old alluvium

Appendix A. Data on Sample Sites, Willcox Basin, 1999--Continued

Sample #	Cadastral	Latitude - Longitude	ADWR #	ADEQ #	Sample Type	Well Depth	Water Depth	Aquifer	Geology
WCX-50	(D-13-25)08dcc	32°18'44.645" 109°48'53.699"	645007	58006	Targeted	167'	130'	Alluvial	Young alluvium
WCX-52	(D-16-24)29dbb	32°00'44.420" 109°55'22.349"	560550	58007	Random	400'	209'	Alluvial	Old alluvium
WCX-53	(D-11-23)12daa	32°29'33.224" 109°56'37.557"	-	58008	Random	800'	346'	Alluvial	Old alluvium
WCX-54	(D-11-24)29caa	32°26'56.584" 109°55'08.844"	617637	58009	Random	1000'	240'	Alluvial	Old alluvium
5th Field Trip, October 13-15, 1999 - Freark & Boettcher (Equipment Blank WCX-61)									
WCX-55	(D-19-29)23acd	31°45'53.144" 109°20'58.955"	-	41954	Random	spring	spring	Hardrock	Metamorphic
WCX-56	(D-17-29)12dab	31°58'09.765" 109°20'28.663"	-	58041	Random	100'	50'	Hardrock	Volcanic
WCX-57/58	(D-18-25)05daa	31°54'04.823" 109°49'29.292"	505828	51698	Random	450'	302'	Alluvial	Old alluvium
WCX-59/60	(D-17-23)25bbd	31°55'53.059" 109°57'40.588"	643215	58042	Random	115'	40'	Hardrock	Granitic
WCX-62	(D-20-29)20ccc	31°40'13.382" 109°24'22.228"	632126	58043	Random	200'	18'	Hardrock	Volcanic
WCX-63	(D-18-24)04aba	31°54'13.321" 109°54'12.838"	510367	58044	Random	652'	590'	Hardrock	Metamorphic
6th Field Trip, November 30 - December 2, 1999 - Freark & Lucci (Equipment Blank WCX-73)									
WCX-64	(D-18-29)14caa	31°52'02.719" 109°21'56.256"	528601	58177	Random	115'	20'	Hardrock	Granitic
WCX-65	(D-13-25)29aba	32°16'55.216" 109°48'58.085	508626	58178	Targeted	82'	43'	Alluvial	Young alluvium
WCX-66/67	(D-13-25)19b	32°17'35.901" 109°50'21.960	646756	58179	Targeted	80'	60'	Alluvial	Young alluvium
WCX-68/69	(D-15-24)16cab	32°07'46.739" 109°54'16.686	616021	49746	Targeted	N/A	N/A	Alluvial	Young alluvium
WCX-70	(D-16-24)10dab	32°03'26.200" 109°53'06.211	-	58180	Random	N/A	N/A	Alluvial	Young alluvium
WCX-71	(D-12-25)36ccc	32°20'29.388" 109°45'20.328	632501	35672	Random	125'	85'	Alluvial	Old alluvium
WCX-72	(D-10-21)33b	32°31'22.510" 110°12'24.282	648403	58181	Random	550'	450'	Hardrock	Volcanic
7th Field Trip, January 12, 2000 - Towne & Flora									
WCX-74	(D-10-24)17dbd	32°33'45.290" 109°54'34.158	615744	34418	Random	720'	520'	Alluvial	Old alluvium

Appendix B. Groundwater Quality Data, Willcox Basin, 1999

Sample #	ADEQ #	MCL Exceedances	Temp. (ºC)	pH-field (su)	SC-lab (FS/cm)	Total Alk (mg/l)	TDS (mg/l)	Hardness (mg/l)	Turbidity (NTU)
WCX-1/2	57854	pH, As, F	22.25	**8.60**	590	140	345	25	0.18
WCX-03	49716	TDS, Alpha	21.42	7.31	1000	330	**600**	380	13.
WCX-04	38111		25.91	7.22	340	120	200	130	0.2
WCX-05	57855		21.04	8.08	350	93	210	130	0.23
WCX-06	57856		20.77	8.24	240	75	140	79	0.31
WCX-08	57856		19.73	8.35	310	51	210	66	0.16
WCX-09	57858	TDS, Cl, SO_4, F	20.02	7.75	1800	200	**1100**	360	0.09
WCX-10	57859		23.80	7.81	410	160	220	130	0.08
WCX-11	57860		19.61	7.68	600	160	310	200	0.12
WCX-12	39827	TDS, SO_4, NO_3	19.66	7.24	1700	260	**1100**	500	0.33
WCX-13	57851		22.18	8.06	380	100	230	85	1.8
WCX-14	57853	Alpha	30.72	7.68	380	180	240	150	11.
WCX-15	57847	As*, F	20.24	8.20	370	130	250	61	0.55
WCX-16	57848	TDS, Alpha	20.79	7.72	790	190	**500**	170	0.38
WCX-1718	57849	TDS, Alpha, Radium	20.90	7.33	1300	280	**730**	345	0.10
WCX-19	57850		19.30	8.01	510	180	290	120	0.18
WCX-20	39117		26.21	7.98	400	160	240	140	0.75
WCX-21	57829		25.12	7.45	430	140	240	140	0.83
WCX-22	57830		23.12	7.56	610	80	380	200	1.4
WCX-23	57831	F	22.84	8.14	260	97	160	54	0.10
WCX-2526	39939		26.94	7.85	260	100	170	76	0.07
WCX-27	57832	F, Fe	22.63	7.95	330	120	210	66	1.5
WCX-28	37833	TDS, NO_3	24.59	7.19	990	190	**630**	350	0.04
WCX-29	41463		23.18	7.71	250	100	160	86	0.05
WCX-3031	57834	TDS, As*	19.81	7.44	1000	210	**585**	295	0.06
WCX-32	58010	TDS, SO_4, NO_3, Sb	19.56	7.43	2200	97	**2100**	910	2.0
WCX-33	58011	pH, As, F	22.21	**9.76**	570	190	420	ND	1.9
WCX-34	58012		21.47	8.24	260	98	180	59	0.18
WCX-35	58013	F, Alpha	20.45	7.54	390	190	260	190	0.19

bold = parameter level exceeds Primary or Secondary MCL ND = not detected above minimum reporting level
* = concentration exceeds the revised arsenic SDW A Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	SAR (value)	Potassium (mg/l)	Bicarbonate (mg/l)	Carbonate (mg/l)	Chloride (mg/l)	Sulfate (mg/l)
WCX-0102	7.9	1.25	115	9.66	1.3	160	4.6	31.5	60
WCX-03	100	33	83	1.84	2.2	400	ND	42	120
WCX-04	36	12	21	0.77	0.88	150	ND	12	20
WCX-05	44	7.1	19	0.70	1.8	110	ND	14	ND
WCX-06	28	3.5	16	0.76	1.4	92	ND	12	ND
WCX-08	27	ND	26	1.36	1.3	62	ND	21	25
WCX-09	69	46	230	5.26	5.0	240	ND	**260**	**270**
WCX-10	46	6.9	38	1.38	2.4	200	ND	9.8	25
WCX-11	61	13	43	1.30	2.8	200	ND	60	29
WCX-12	180	15	160	3.08	4.1	320	ND	44	**490**
WCX-13	33	1.9	43	1.97	2.1	120	ND	14	43
WCX-14	56	6.8	25	0.84	4.3	220	ND	5.3	ND
WCX-15	23	2.1	58	3.10	2.0	160	ND	9.5	24
WCX-16	59	8.9	94	3.02	1.3	230	ND	62	88
WCX-1718	99	25.5	135	2.99	4.1	340	ND	175	93.5
WCX-19	35	8.8	69	2.70	1.5	220	ND	26	35
WCX-20	45	6.8	30	1.10	2.0	200	ND	8.3	31
WCX-21	42	9.2	29	1.05	2.1	170	ND	22	18
WCX-22	76	6.1	31	0.92	2.6	98	ND	32	150
WCX-23	20	1.1	34	2.00	1.2	120	ND	5.7	ND
WCX-2526	30	1.0	24	1.17	1.4	120	ND	3.75	13.5
WCX-27	23	2.2	46	2.45	1.8	150	ND	6.4	25
WCX-28	100	23	65	1.53	4.1	230	ND	55	170
WCX-29	35	1.9	16	0.72	1.3	120	ND	5.5	ND
WCX-3031	91	16	87	2.21	2.8	260	ND	125	64
WCX-32	370	38	160	2.12	4.3	120	ND	140	**1000**
WCX-33	ND	ND	140	21.53	0.82	110	61	24	51
WCX-34	17	2.6	33	1.96	0.80	120	ND	12	ND
WCX-35	52	14	18	0.57	1.8	230	ND	4.6	20

bold = parameter level exceeds Primary or Secondary MCL

ND = not detected above minimum reporting level

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	Nitrate-Nitrite-N (mg/l)	Nitrate - N (mg/l)	Nitrite-N (mg/l)	TKN (mg/l)	Ammonia-N (mg/l)	Phosphorus (mg/l)
WCX-01/02	1.3	1.3	ND	ND	ND	ND
WCX-03	3.6	3.6	ND	ND	ND	0.054
WCX-04	0.94	0.94	ND	ND	ND	0.079
WCX-05	8.4	8.4	ND	ND	ND	ND
WCX-06	2.0	2.0	ND	ND	ND	ND
WCX-08	3.4	3.4	ND	ND	ND	ND
WCX-09	0.67	0.67	ND	ND	ND	ND
WCX-10	0.60	0.60	ND	ND	ND	ND
WCX-11	1.3	1.3	ND	ND	ND	ND
WCX-12	**13**	**13**	ND	0.19	ND	ND
WCX-13	0.68	0.68	ND	ND	ND	ND
WCX-14	0.2	0.2	ND	0.078	0.021	ND
WCX-15	0.7	0.7	ND	0.078	ND	ND
WCX-16	4.3	4.3	ND	0.053	ND	ND
WCX-17/18	8.0	8.0	ND	0.18	ND	ND
WCX-19	0.38	0.38	ND	ND	ND	ND
WCX-20	0.58	0.58	ND	ND	ND	ND
WCX-21	1.8	1.8	ND	ND	ND	ND
WCX-22	1.1	1.1	ND	ND	ND	ND
WCX-23	0.56	0.56	ND	0.11	ND	ND
WCX-25/26	0.23	0.23	ND	ND	ND	ND
WCX-27	0.57	0.57	ND	ND	ND	ND
WCX-28	**14**	**14**	ND	0.17	ND	ND
WCX-29	0.51	0.51	ND	ND	ND	ND
WCX-30/31	8.5	8.5	ND	0.145	ND	ND
WCX-32	**15**	**15**	ND	0.32	ND	ND
WCX-33	0.36	0.36	ND	0.073	ND	ND
WCX-34	0.57	0.57	ND	0.13	ND	ND
WCX-35	0.095	0.095	ND	0.086	ND	ND

bold = parameter level exceeds Primary or Secondary MCL   ND = not detected above minimum reporting level

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	Antimony (mg/l)	Arsenic (mg/l)	Barium (mg/l)	Beryllium (mg/l)	Boron (mg/l)	Cadmium (mg/l)	Chromium (mg/l)	Copper (mg/l)	Fluoride (mg/l)
WCX-01/02	ND	**0.74**	ND	ND	0.12	ND	ND	ND	**7.05**
WCX-03	ND	ND	ND	ND	ND	ND	ND	ND	0.75
WCX-04	ND	ND	ND	ND	ND	ND	ND	ND	0.56
WCX-05	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-06	ND	ND	ND	ND	ND	ND	ND	ND	0.32
WCX-08	ND	ND	ND	ND	ND	ND	ND	ND	0.33
WCX-09	ND	0.033	ND	ND	0.25	ND	ND	ND	**3.8**
WCX-10	ND	ND	ND	ND	ND	ND	ND	ND	1.2
WCX-11	ND	ND	0.17	ND	ND	ND	ND	ND	0.75
WCX-12	ND	ND	ND	ND	0.58	ND	ND	ND	1.3
WCX-13	ND	ND	ND	ND	0.15	ND	ND	ND	1.8
WCX-14	ND	ND	ND	ND	ND	ND	ND	0.025	0.47
WCX-15	ND	0.016*	ND	ND	ND	ND	0.019	ND	**4.7**
WCX-16	ND	ND	ND	ND	0.15	ND	ND	ND	0.90
WCX-17/18	ND	ND	ND	ND	0.14	ND	ND	ND	1.5
WCX-19	ND	ND	ND	ND	ND	ND	ND	ND	1.1
WCX-20	ND	ND	ND	ND	ND	ND	0.033	ND	0.90
WCX-21	ND	ND	0.11	ND	ND	ND	0.017	ND	1.1
WCX-22	ND	ND	ND	ND	ND	ND	ND	ND	0.39
WCX-23	ND	ND	ND	ND	ND	ND	ND	ND	**2.5**
WCX-25/26	ND	ND	ND	ND	ND	ND	ND	ND	1.05
WCX-27	ND	ND	ND	ND	0.22	ND	ND	ND	**4.0**
WCX-28	ND	ND	ND	ND	0.12	ND	ND	0.013	1.4
WCX-29	ND	ND	ND	ND	ND	ND	ND	0.019	0.44
WCX-30/31	ND	0.010*	ND	ND	0.11	ND	ND	ND	0.945
WCX-32	**0.0090**	ND	ND	.00064	0.14	ND	ND	ND	0.40
WCX-33	ND	**0.1**	ND	ND	0.19	ND	ND	ND	**10**
WCX-34	ND	ND	ND	ND	ND	ND	ND	ND	1.1
WCX-35	ND	ND	ND	ND	ND	ND	ND	0.014	**2.2**

bold = parameter level exceeds Primary or Secondary MCL   ND = not detected above minimum reporting level

* = concentration exceeds the revised arsenic SDWA Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	Iron (mg/l)	Lead (mg/l)	Manganese (mg/l)	Mercury (mg/l)	Nickel (mg/l)	Selenium (mg/l)	Silver (mg/l)	Thallium (mg/l)	Zinc (mg/l)
WCX-01/02	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-03	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-04	ND	ND	ND	ND	ND	ND	ND	ND	0.47
WCX-05	ND	ND	ND	ND	ND	ND	ND	ND	0.25
WCX-06	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-08	ND	ND	ND	ND	ND	0.0061	ND	ND	ND
WCX-09	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-10	ND	ND	ND	ND	ND	0.006	ND	ND	ND
WCX-11	ND	ND	ND	ND	ND	ND	ND	ND	0.13
WCX-12	ND	ND	ND	ND	ND	ND	ND	ND	0.057
WCX-13	ND	ND	ND	ND	ND	ND	ND	ND	0.36
WCX-14	ND	ND	ND	ND	0.025	0.0081	ND	ND	0.089
WCX-15	ND	ND	ND	ND	ND	ND	ND	ND	0.085
WCX-16	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-17/18	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-19	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-20	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-21	ND	ND	ND	ND	ND	ND	ND	ND	0.29
WCX-22	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-23	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-25/26	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-27	**0.42**	ND	ND	ND	ND	ND	ND	ND	0.22
WCX-28	0.10	ND	ND	ND	0.013	0.01	ND	ND	0.062
WCX-29	ND	ND	ND	ND	0.019	ND	ND	ND	0.29
WCX-30/31	ND	ND	ND	ND	ND	ND	0.0058	ND	0.58
WCX-32	ND	ND	ND	ND	ND	ND	ND	ND	0.41
WCX-33	ND	ND	ND	ND	ND	ND	0.0058	ND	0.75
WCX-34	ND	ND	ND	ND	ND	ND	0.0081	ND	0.97
WCX-35	0.17	ND	ND	ND	0.014	ND	0.012	ND	0.23

bold = parameter level exceeds Primary or Secondary MCL

ND = not detected above minimum reporting level

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	Gross Alpha (pCi/L)	Gross Beta (pCi/L)	Ra-226 (pCi/L)	Ra-228 (pCi/L)	Uranium (ug/l)	d15 N (⁰/₀₀)	VOC (ug/l)	GWPL pesticide	Type of Chemistry
WCX-01/02	< LLD	< 1.4+/-0.9	-	-	-	-	ND	-	sodium-mixed
WCX-03	**29+/-1.3**	16+/-1.2	< LLD	-	**25+/-1.8**	-	ND	-	mixed-bicarbonate
WCX-04	< LLD	< LLD	-	-	-	-	ND	-	mixed-bicarbonate
WCX-05	1.2+/-0.56	1.7+/-0.9	-	-	-	10.5	ND	-	calcium-bicarbonate
WCX-06	1.4+/-0.44	2.4+/-0.88	-	-	-	-	ND	-	calcium-bicarbonate
WCX-08	0.78+/-0.48	< LLD	-	-	-	-	ND	-	calcium-mixed
WCX-09	8.9+/-0.92	6.9+/-1.2	< LLD	-	-	-	ND	-	sodium-mixed
WCX-10	-	-	-	-	-	-	ND	-	calcium-bicarbonate
WCX-11	5.2+/-0.94	3.6+/-0.92	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-12	-	-	-	-	-	5.11	ND	-	calcium-sulfate
WCX-13	5.1+/-0.76	2.7+/-0.92	< LLD	-	3.5+/-0.08	-	ND	-	sodium-bicarbonate
WCX-14	**15+/-1.6**	12+/-1.1	< LLD	-	1.7+/-0.28	-	ND	-	calcium-bicarbonate
WCX-15	3.0+/-0.72	1.7+/-0.86	-	-	-	-	ND	-	sodium-bicarbonate
WCX-16	**15+/-1.1**	4.6+/-0.98	< LLD	-	18+/-0.48	-	ND	-	sodium-mixed
WCX-17/18	**239+/-3.8**	88+/-4.50	**17+/-1**	**10.2+/-1.3**	**232+/-17**	16.2	ND	-	mixed-mixed
WCX-19	5.4+/-0.9	3.6+/-0.94	< LLD	-	-	-	ND	-	sodium-bicarbonate
WCX-20	6.5+/-0.9	4.6+/-0.9	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-21	2.0+/-0.64	2.4+/-0.92	-	-	-	-	ND	-	calcium-bicarbonate
WCX-22	2.5+/-0.72	3.0+/-0.94	-	-	-	-	ND	-	calcium-sulfate
WCX-23	6.1+/-0.76	2.7+/-0.84	< LLD	-	-	-	ND	-	sodium-bicarbonate
WCX-25/26	5.45+/-0.77	2.5+/-0.87	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-27	5.9+/-0.86	2.4+/-0.94	< LLD	-	-	-	ND	-	sodium-bicarbonate
WCX-28	9.3+/-0.88	5.0+/-0.96	< LLD	-	-	8.25	ND	-	calcium-mixed
WCX-29	2.8+/-0.62	< LLD	-	-	-	-	ND	-	calcium-bicarbonate
WCX-30/31	4.5+/-0.82	4.1+/-0.98	-	-	-	10.2	ND	-	mixed-mixed
WCX-32	3.7+/-0.56	8.4+/-1.7	-	-	-	5.43	ND	ND	calcium-sulfate
WCX-33	4.6+/-1.0	< LLD	-	-	-	-	ND	ND	sodium-bicarbonate
WCX-34	1.6+/-0.58	< LLD	-	-	-	-	ND	ND	sodium-bicarbonate
WCX-35	**16+/-1.5**	3.2+/-0.94	< LLD	-	13+/-0.44	-	ND	-	calcium-bicarbonate

bold = parameter level exceeds Primary or Secondary MCL
ND = not detected above minimum reporting level
LLD = Lower Limit of Detection

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	ADEQ #	MCL Exceedances	Temp. (°C)	pH-field (su)	SC-lab (FS/cm)	Total Alk. (mg/l)	TDS (mg/l)	Hardness (mg/l)	Turbidity (NTU)
WCX-36	58014		9.45	7.32	130	73	78	65	0.63
WCX-37	--		7.05	5.83	41	10	46	17	0.16
WCX-38/39	58015	F, Alpha	18.37	6.84	275	110	215	97.5	1.05
WCX-41	58016		25.64	7.87	390	85	290	140	0.84
WCX-42	58000		23.63	7.82	200	95	150	77	0.10
WCX-43	41944		25.71	8.02	240	120	180	84	0.10
WCX-44/45	58001	pH, As*, F	22.47	**8.68**	735	140	490	27	2.1
WCX-46	58002		20.95	8.25	270	88	200	79	0.24
WCX-47	58003		24.78	7.37	450	200	290	200	4.4
WCX-48	58004	NO_3,	26.01	7.75	580	160	370	240	0.30
WCX-49	58005		25.27	7.70	440	160	280	200	0.50
WCX-50	58006	pH, As, F	22.52	**9.63**	560	170	370	ND	0.56
WCX-52	58007		22.10	7.50	450	220	280	220	1.8
WCX-53	58008		23.02	8.01	190	91	140	81	0.05
WCX-54	58009		22.12	7.99	270	73	190	86	0.18
WCX-55	41954		18.49	6.68	670	310	420	330	0.34
WCX-56	58041	Mn	16.84	7.12	640	230	450	320	4.0
WCX-57/58	51698		26.53	7.18	465	180	300	200	0.16
WCX-59/60	58042	F, Alpha	19.83	6.57	510	160	360	205	0.77
WCX-62	58043		18.38	6.63	720	310	470	330	0.08
WCX-63	58044		23.62	7.33	370	160	230	180	0.30
WCX-64	58177		16.67	7.19	260	110	160	110	0.33
WCX-65	58178	TDS, As*, F	18.38	7.46	990	300	**580**	150	0.17
WCX-66/67	58179	As*, F	19.93	8.13	415	110	255	73.5	0.22
WCX-68/69	49746	TDS, Cl, SO_4,	18.65	7.46	1800	170	**1050**	410	0.22
WCX-70	58180		20.84	7.54	800	150	420	320	0.20
WCX-71	35672	TDS, NO_3,	19.92	7.08	1500	260	**850**	560	1.2
WCX-72	58181		23.58	7.80	140	60	130	21	5.4
WCX-74	--		24.60	7.52	380	150	240	150	1.8

bold = parameter level exceeds Primary or Secondary MCL   ND = not detected above minimum reporting level
* = concentration exceeds the revised arsenic SDWA Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	SAR (value)	Potassium (mg/l)	Bicarbonate (mg/l)	Carbonate (mg/l)	Chloride (mg/l)	Sulfate (mg/l)
WCX-36	19	3.5	6.0	0.33	ND	89	ND	1.8	ND
WCX-37	ND	ND	ND	0.39	ND	12	ND	1.2	ND
WCX-38/39	34	1.6	21.5	0.97	1.1	130	ND	4.2	20
WCX-41	52	2.4	31	1.14	2.7	100	ND	11	99
WCX-42	26	4.0	15	0.72	1.3	120	ND	4.0	ND
WCX-43	32	2.3	23	1.06	1.5	150	ND	3.6	ND
WCX-44/45	9.1	1.35	150	12.11	1.25	160	5.7	60	96
WCX-46	28	3.1	28	1.34	1.4	110	ND	6.8	15
WCX-47	69	10	20	0.60	1.4	240	ND	14	15
WCX-48	47	31	32	0.89	2.8	200	ND	31	50
WCX-49	48	22	18	0.54	2.0	200	ND	7.3	56
WCX-50	ND	ND	130	19.98	1.3	100	50	22	43
WCX-52	46	25	19	0.56	2.0	270	ND	6.5	14
WCX-53	28	3.9	13	0.61	1.2	110	ND	3.9	ND
WCX-54	32	2.5	21	0.96	1.3	89	ND	27	ND
WCX-55	130	8.7	17	0.39	0.86	380	ND	7.5	44
WCX-56	110	17	15	0.35	1.4	280	ND	5.6	120
WCX-57/58	64	12	23	0.69	3.65	220	ND	10	58.5
WCX-59/60	64	11.5	28.5	0.86	0.72	200	ND	18.5	85
WCX-62	100	21	36	0.86	1.1	380	ND	13	73
WCX-63	58	11	9.1	0.29	1.5	200	ND	3.0	21
WCX-64	39	4.6	9.7	0.39	0.58	130	ND	3.0	15
WCX-65	42	11	170	6.03	3.1	370	ND	60	86
WCX-66/67	24.5	3.45	60.5	0.76	1.8	130	ND	23	45
WCX-68/69	85.5	47.5	220	4.75	5.8	210	ND	**290**	**285**
WCX-70	75	34	31	0.75	2.6	180	ND	110	63
WCX-71	140	48	93	1.73	1.0	320	ND	230	85
WCX-72	7.3	ND	23	2.24	4.9	73	ND	5.1	ND
WCX-74	42	12	23	0.80	1.6	180	ND	13	16

bold = parameter level exceeds Primary or Secondary MCL

ND = not detected above minimum reporting level

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	Nitrate-Nitrite-N (mg/l)	Nitrate - N (mg/l)	Nitrite-N (mg/l)	TKN (mg/l)	Ammonia-N (mg/l)	Phosphorus (mg/l)
WCX-36	0.075	0.075	ND	0.064	ND	ND
WCX-37	ND	ND	ND	0.13	ND	ND
WCX-38/39	0.14	0.14	ND	0.12	ND	ND
WCX-41	0.62	0.62	ND	ND	ND	ND
WCX-42	0.45	0.45	ND	ND	ND	ND
WCX-43	0.35	0.35	ND	ND	ND	ND
WCX-44/45	2.35	2.35	ND	0.058	ND	ND
WCX-46	4.5	4.5	ND	ND	ND	ND
WCX-47	0.53	0.53	ND	ND	ND	ND
WCX-48	**12**	**12**	ND	ND	ND	ND
WCX-49	1.1	1.1	ND	0.14	ND	ND
WCX-50	0.40	0.40	ND	0.084	ND	ND
WCX-52	1.0	1.0	ND	0.091	ND	ND
WCX-53	0.76	0.76	ND	0.24	ND	ND
WCX-54	4.5	4.5	ND	0.14	ND	ND
WCX-55	0.18	0.18	ND	ND	ND	ND
WCX-56	ND	ND	ND	0.10	ND	ND
WCX-57/58	0.265	0.265	ND	ND	ND	ND
WCX-59/60	0.076	0.076	ND	0.084	ND	ND
WCX-62	0.093	0.093	ND	0.11	ND	ND
WCX-63	1.4	1.4	ND	ND	ND	ND
WCX-64	0.024	0.024	ND	0.081	ND	ND
WCX-65	8.7	8.7	ND	0.19	ND	ND
WCX-66/67	0.73	0.73	ND	ND	ND	ND
WCX-68/69	0.78	0.78	ND	ND	ND	ND
WCX-70	2.9	2.9	ND	0.20	ND	ND
WCX-71	**18**	**18**	ND	0.21	ND	0.065
WCX-72	0.42	0.42	ND	0.07	ND	ND
WCX-74	0.67	0.67	ND	ND	ND	0.032

bold = parameter level exceeds Primary or Secondary MCL

ND = not detected above minimum reporting level

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	Antimony (mg/l)	Arsenic (mg/l)	Barium (mg/l)	Beryllium (mg/l)	Boron (mg/l)	Cadmium (mg/l)	Chromium (mg/l)	Copper (mg/l)	Fluoride (mg/l)
WCX-36	ND	ND	ND	ND	ND	ND	ND	ND	0.45
WCX-37	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-38/39	ND	ND	ND	ND	ND	ND	ND	0.031	**2.6**
WCX-41	ND	ND	ND	ND	0.12	ND	0.014	ND	0.57
WCX-42	ND	ND	ND	ND	ND	ND	ND	ND	0.45
WCX-43	ND	ND	ND	ND	ND	ND	ND	ND	0.49
WCX-44/45	ND	0.0465*	ND	ND	0.14	ND	ND	ND	**7.6**
WCX-46	ND	ND	ND	ND	ND	ND	0.032	ND	1.1
WCX-47	ND	ND	0.35	ND	ND	ND	ND	ND	0.47
WCX-48	ND	ND	ND	ND	ND	ND	ND	ND	1.2
WCX-49	ND	ND	ND	ND	ND	ND	ND	ND	0.71
WCX-50	ND	**0.065**	ND	ND	0.12	ND	ND	ND	**10**
WCX-52	ND	ND	0.24	ND	ND	ND	0.042	ND	0.48
WCX-53	ND	ND	ND	ND	ND	ND	0.013	ND	0.42
WCX-54	ND	ND	ND	ND	ND	ND	ND	ND	0.25
WCX-55	ND	ND	0.31	ND	ND	ND	ND	ND	0.21
WCX-56	ND	ND	ND	ND	ND	ND	ND	ND	0.70
WCX-57/58	ND	ND	ND	ND	ND	ND	ND	ND	0.66
WCX-59/60	ND	ND	ND	.00073	ND	ND	ND	ND	**2.1**
WCX-62	ND	ND	ND	ND	ND	ND	ND	ND	0.36
WCX-63	ND	ND	ND	ND	ND	ND	ND	ND	1.1
WCX-64	ND	ND	ND	ND	ND	ND	ND	ND	0.68
WCX-65	ND	0.025*	ND	ND	0.21	ND	ND	ND	**4.4**
WCX-66/67	ND	0.011*	ND	ND	ND	ND	ND	ND	**5.0**
WCX-68/69	ND	ND	ND	ND	0.13	ND	ND	ND	1.3
WCX-70	ND	ND	0.25	ND	ND	ND	ND	ND	0.62
WCX-71	ND	ND	ND	ND	0.16	ND	ND	ND	1.2
WCX-72	ND	ND	ND	ND	ND	ND	ND	ND	0.37
WCX-74	ND	ND	ND	ND	ND	ND	ND	ND	1.2

bold = parameter level exceeds Primary or Secondary MCL   ND = not detected above minimum reporting level
* = concentration exceeds the revised arsenic SDWA Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, Willcox Basin, 1999--Continued

Sample #	Iron (mg/l)	Lead (mg/l)	Manganese (mg/l)	Mercury (mg/l)	Nickel (mg/l)	Selenium (mg/l)	Silver (mg/l)	Thallium (mg/l)	Zinc (mg/l)
WCX-36	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-37	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-38/39	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-41	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-42	ND	ND	ND	ND	ND	ND	ND	ND	0.085
WCX-43	ND	ND	ND	ND	ND	ND	ND	ND	0.11
WCX-44/45	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-46	ND	ND	ND	ND	ND	ND	ND	ND	0.084
WCX-47	ND	ND	ND	ND	ND	ND	ND	ND	0.29
WCX-48	ND	ND	ND	ND	ND	ND	ND	ND	0.098
WCX-49	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-50	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-52	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-53	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-54	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-55	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-56	0.22	ND	**0.14**	ND	ND	ND	ND	ND	0.070
WCX-57/58	ND	ND	ND	ND	ND	ND	ND	ND	0.265
WCX-59/60	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-62	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-63	ND	ND	ND	ND	ND	ND	ND	ND	0.30
WCX-64	ND	ND	ND	ND	ND	ND	ND	ND	ND
WCX-65	ND	ND	ND	ND	ND	0.022	ND	ND	ND
WCX-66/67	ND	ND	ND	ND	ND	0.0055	ND	ND	ND
WCX-68/69	ND	ND	ND	ND	ND	0.0057	ND	ND	0.16
WCX-70	ND	ND	ND	ND	ND	0.015	ND	ND	ND
WCX-71	ND	ND	ND	ND	ND	0.012	ND	ND	0.27
WCX-72	0.13	ND	ND	ND	ND	ND	ND	ND	0.25
WCX-74	ND	ND	ND	ND	ND	ND	ND	ND	0.065

bold = parameter level exceeds Primary or Secondary MCL   ND = not detected above minimum reporting level

Appendix B. Groundwater Quality Data, Willcox Basin 1999--Continued

Sample #	Gross Alpha (pCi/L)	Gross Beta (pCi/L)	Ra-226 (pCi/L)	Ra-228 (pCi/L)	Uranium (ug/l)	d^{15} N ($^0/_{00}$)	VOC (ug/l)	GWPL pesticide	Type of Chemistry
WCX-36	11+/-1.0	0.82+/-0.88	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-37	1.1+/-0.46	< LLD	-	-	-	-	ND	-	calcium-bicarbonate
WCX-38/39	**24+/-1.6**	1.95+/-0.93	< LLD	-	10.1+/-0.32	-	ND	-	calcium-bicarbonate
WCX-41	3.6+/-0.76	4.0+/-0.90	-	-	-	-	ND	ND	calcium-sulfate
WCX-42	5.0+/-0.72	1.8+/-0.90	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-43	4.7+/-0.88	1.5+/-0.86	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-44/45	2.2+/-0.80	1.6+/-0.96	-	-	-	-	ND	-	sodium-mixed
WCX-46	2.2+/-0.58	1.7+/-0.84	-	-	-	-	ND	-	mixed-bicarbonate
WCX-47	5.9+/-0.98	2.4+/-0.96	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-48	7.2+/-1.2	3.1+/-1.0	< LLD	-	-	8.72	ND	-	mixed-bicarbonate
WCX-49	4.7+/-0.84	2.3+/-0.88	-	-	-	-	ND	-	mixed-bicarbonate
WCX-50	2.2+/-0.68	< LLD	-	-	-	-	ND	-	sodium-mixed
WCX-52	6.8+/-1.1	2.3+/-0.98	< LLD	-	-	-	ND	-	mixed-bicarbonate
WCX-53	1.7+/-0.68	1.7+/-0.86	-	-	-	-	ND	-	calcium-bicarbonate
WCX-54	1.6+/-0.68	1.6+/-0.68	-	-	-	-	ND	-	calcium-bicarbonate
WCX-55	14+/-1.1	< LLD	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-56	6.1+/-0.82	2.3+/-0.92	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-57/58	10+/-1.2	6.7+/-1.0	< LLD	-	2.3+/-0.08	-	ND	-	calcium-bicarbonate
WCX-59/60	**62+/-2.6**	19+/-1.2	< LLD	-	17+/-0.6	-	YES	-	calcium-bicarbonate
WCX-62	3.0+/-0.72	< LLD	-	-	-	-	ND	-	calcium-bicarbonate
WCX-63	2.0+/-0.68	2.4+/-0.9	-	-	3.3+/-0.14	-	ND	-	calcium-bicarbonate
WCX-64	15+/-1.1	5.2+/-0.98	< LLD	-	-	-	ND	-	calcium-bicarbonate
WCX-65	-	-	-	-	-	-	ND	-	sodium-bicarbonate
WCX-66/67	-	-	-	-	-	-	ND	-	sodium-bicarbonate
WCX-68/69	-	-	-	-	-	-	ND	-	sodium-mixed
WCX-70	-	-	-	-	-	-	ND	-	mixed-mixed
WCX-71	9.6+/-0.92	1.7+/-1.0	< LLD	-	-	-	ND	-	mixed-mixed
WCX-72	0.93+/-0.48	4.6+/-0.88	-	-	-	-	ND	-	sodium-bicarbonate
WCX-74	6.6+/-0.98	4.6+/-0.90	< LLD	-	-	-	ND	-	calcium-bicarbonate

bold = parameter level exceeds Primary or Secondary MCL   ND = Not detected above minimum reporting level
LLD = Lower Limit of Detection

Appendix C. Volatile Organic Compounds (VOCs) SDW 502.2 Analyte List

Benzene	1,2-Dichloroethene	1,1,2-Trichloroethane
Bromozene	1,1-Dichloroethene	Trichloroethene
Bromochloromethane	cis-1,2-Dichloroethene *	Trichlorofluormethane
Bromodichloromethane	trans-1,2-Dichlorothene *	1,2,3-Trichloropropane
Bromoform	1,2-Dichloropropane	1,2,4-Trimethylbenzene
Bromomethane	1,3-Dichloropropane	1,3,5-Trimethylbenzene
n-Butylbenzene	2,2-Dichloropropane	Vinyl Chloride
sec-Butylbenzene	1,1-Dichloropropene	Total Xylenes
tert-Butylbenzene	c-1,3-Dichloropropene	Methyl-t-butyl ether (MTBE)
Carbon Tetrachloride	t-1,3-Dichloropropene	
Chlorobenzene	Ethylbenzene	
Chloroethane	Hexachlorobutadiene	
Chloroform	Isopropylbenzene	
Chloromethane	p-Isopropyltoluene	
2-Chlorotoluene	Methylene Chloride	
4-Chlorotoluene	Naphthalene	
Dibromochloromethane	n-Propylbenzene	
1,2-Dibromo-3-chloropropane	Styrene	
1,2-Dibromoethane	1,1,1,2-Tetrachloroethane	
Dibromomethane	1,1,2,2-Tetrachloroethane	
1,2-Dichlorobenzene	Tetrachloroethene	
1,3-Dichlorobenzene	Toluene	
1,4-Dichlorobenzene	1,2,3-Trichlorobenzene	
Dichlorodifluormethane	1,2,4-Trichlorobenzene	
1,1-Dichloroethane	1,1,1-Trichlorobenzene	

All Minimum Reporting Limits are 0.5 Fg/l except those marked with an asterisk (*) which are 0.25 Fg/l
VOCs from sites WCX-1- 41 and WCX-74 were analyzed at the ADHS laboratory using the above 502.2 analyte list
Source: ADHS Laboratory

Appendix D. MRLs of Volatile Organic Compounds (VOCs) on the EPA 8260B Analyte List

Acetone - 20	1,2-Dichloroethene - 2	1,1,1-Trichlorobenzene - 2
Benzene - 2	1,1-Dichloroethene - 5	1,1,2-Trichloroethane - 2
Bromobenzene - 5	cis-1,2-Dichloroethene - 2	Trichloroethene - 2
Bromochloromethane - 5	trans-1,2-Dichlorothene - 5	Trichlorofluormethane - 5
Bromodichloromethane - 2	1,2-Dichloropropane - 2	1,2,3-Trichloropropane - 10
Bromoform - 5	1,3-Dichloropropane - 2	1,2,4-Trimethylbenzene - 2
Bromomethane - 5	2,2-Dichloropropane - 2	1,3,5-Trimethylbenzene - 2
2-Butanone (MEK) - 10	1,1-Dichloropropene - 2	Vinyl Acetate - 5
n-Butylbenzene - 5	c-1,3-Dichloropropene - 2	Vinyl Chloride - 5
sec-Butylbenzene - 5	t-1,3-Dichloropropene - 2	Total Xylenes - 10
tert-Butylbenzene - 5	Ethylbenzene - 2	
Carbon Disulfide - 5	Hexachlorobutadiene - 5	
Carbon tetrachloride - 5	2-Hexanone - 10	
Chlorobenzene - 2	Iodomethane - 2	
Chloroethane - 5	Isopropylbenzene - 2	
Chloroform - 2	p-Isopropyltoluene - 2	
Chloromethane - 5	Methylene Chloride - 5	
2-Chlorotoluene - 5	4-Methyl-2-pentanone (MIBK) - 10	
4-Chlorotoluene - 5	Methyl-t-butyl ether (MTBE) - 5	
Dibromochloromethane - 2	Naphthalene - 5	
1,2-Dibromo-3-chloropropane - 5	n-Propylbenzene - 2	
1,2-Dibromoethane (EDB) - 2	Styrene - 2	
Dibromomethane - 2	1,1,1,2-Tetrachloroethane - 5	
1,2-Dichlorobenzene - 2	1,1,2,2-Tetrachloroethane - 2	
1,3-Dichlorobenzene - 2	Tetrachloroethene - 2	
1,4-Dichlorobenzene - 2	Toluene - 2	
Dichlorodifluormethane - 5	1,2,3-Trichlorobenzene - 5	
1,1-Dichloroethane - 2	1,2,4-Trichlorobenzene - 5	

All Minimum Reporting Limits are in µg/l
VOC samples at sites WCX-42 through 72 were analyzed using the above 8260B analyte list
Source: Del Mar Laboratory.

Appendix E. MRLs of Groundwater Protection List (GWPL) Pesticides

GWPL Carbamates

Aldicarb - 1

Carbaryl - 1

Carbofuran - 1

Methiocarb - 1

Methomyl - 1

Oxamyl - 1

GWPL Herbicides

2,4-D - 0.5

Dacthal (Acids) - 0.5

Dicamba - 0.5

GWPL Pesticides

Ametryn - 10

Azinphos-methyl - 10

Bromacil - 10

Butylate - 10

Captan - 25

Carboxin - 5

Chlorothalonil - 5

Cyanazine - 10

Cycloate - 5

Dacthal - 5

Diazinon - 10

Dichloran - 10

Diethatyl ethyl - 10

Dimethoate - 10

Diphenamid - 5

Diuron (Fragment) - 10

DPX-M6316 - 25

Endosulfan - 10

EPTC - 5

Ethofumesate - 10

Ethoprop - 10

Fenamiphos - 25

Fenarimol - 5

Fluazifop-p-butyl - 10

Flucythrinate - 10

Fluometuron (Fragment) - 10

Fluridone - 10

Hexazinone - 5

Imazalil - 10

Isaazophos - 10

Linuron - 10

Metalaxyl - 10

Metaldehyde - 5

Methyl Parathion - 10

Metolachlor - 5

Metribuzin - 10

Mevinphos - 10

Myclobutanil - 10

Napropamide - 5

Norflurazon - 10

Parathion - 10

Pebulate - 5

Permethrin - 5

Phosmet - 10

Phosphamidon - 5

Piperonyl Butoxide - 10

Profenofos - 25

Prometon - 10

Prometryn - 10

Pronamide - 10

Propiconazole - 10

Pyrazon - 10

Sethoxydim (Fragment) - 10

Sulfometuron-methyl - 10

Sulprofos - 10

Tebuthiuron - 25

Terbacil - 5

Terbufos - 10

Thidiazuron (Fragment) - 10

Triadimefon - 10

Vernolate - 5

Vinclozolin - 10

GWPL Pesticides - SIM

Alachlor - 1

Atrazine - 1

Lindane 0.1

Simzine - 1

All units in Fg/l
Source: ADHS Laboratory.

Appendix E. INVESTIGATION METHODS

Various groundwater sites were sampled by the ADEQ Groundwater Monitoring Program to characterize regional groundwater quality in the WGB. Samples were collected at all sites for SDW inorganics (physical parameters, major ions, nutrients, and trace elements) analyses. At most sites, SDW VOCs and SDW radiochemistry samples were collected for analysis. At limited sites, samples were collected for nitrogen isotope and GWPL pesticide analyses.   No bacteria sampling was conducted since microbiological contamination problems in groundwater are often transient and subject to a variety of changing environmental conditions including soil moisture content and temperature.[22]

Sampling Strategy

This study focused on groundwater quality conditions that are large in scale and persistent in time. This research is designed to identify regional degradation of groundwater quality such as occurs from non-point sources of pollution or a high density of point sources.

The quantitative estimation of regional groundwater quality conditions requires the selection of sampling locations that follow scientific principles for probability sampling. Thus, sampling in the WGB conducted by ADEQ follows a systematic grid-based, random site-selection approach. This is an efficient method because it requires sampling relatively few sites to make valid statistical statements about the condition of large areas. This systematic element requires that the selected wells be spatially distributed while the random element ensures that every well within a cell has an equal chance of being sampled. This strategy also reduces the possibility of biased well selection and assures adequate spatial coverage throughout the study area. The main benefit of a statistically-designed sampling plan is that it allows much greater groundwater quality assumptions than would be allowable with a non-statistical approach.

The U.S. Public Land Survey System was used as a grid overlay to subdivide the WGB into six, square-mile townships. Within each township, a well from the ADWR database was randomly selected to sample. Wells pumping groundwater for a variety of purposes - domestic, stock, and irrigation - were sampled for this study, provided each well met ADEQ requirements.

A well was considered suitable for sampling if the well owner gave permission to sample, if a sampling point existed near the wellhead, and if the well casing and surface seal appeared to be intact and undamaged. Other factors such as well casing access to determine groundwater depth and construction information were preferred but not considered essential.

If no registered wells were available within a township, springs or unregistered wells were randomly selected for sampling. Springs were considered adequate for sampling if they had a constant flow through a clearly-defined point of egress, and if the sample point had minimal surface impacts. Well information compiled from the ADWR well registry and spring characteristics are provided in **Appendix A**.

Several factors were considered to determine sample size for this study. Aside from administrative limitations on funding and personnel, this decision was based on three factors related to the conditions in the area:[25]

- Amount of groundwater quality data already available,
- Extent to which impacted groundwater is known or believed likely to occur, and
- Hydrologic complexity and variability of the area.

Sample Collection

The personnel who designed the WGB study were also responsible for the collection and interpretation of the data.[17] This protocol helps ensure that consistently high quality data are collected, from which are drawn relevant and meaningful interpretations. The sample collection methods for this study conformed to the *Quality Assurance Project Plan (QAPP)*[2] and the *Field Manual For Water Quality Sampling*.[7] While these sources should be consulted as references to specific sampling questions, a brief synopsis of the procedures involved in collecting a groundwater sample is provided.

After obtaining permission from the owner to sample the well, the water level was measured with a sounder if the casing had access for a probe. The volume of water needed to purge the well three bore hole volumes was calculated from well log and on-site information. Physical parameters - temperature, pH, and specific conductivity - were monitored at least every five minutes using a Hydrolab multi-parameter instrument. Typically, after three bore volumes had been pumped and the physical parameters were stabilized within 10 percent, a sample representative of the aquifer was collected from a point as close to the wellhead as possible. In certain instances, it was not possible to purge three bore volumes. In these cases, at least one bore volume was evacuated and the physical parameters had stabilized within 10 percent.

Sample bottles were filled in the following order:

1. VOCs,
2. Pesticides,
3. Inorganic Constituents,
4. Nitrogen isotopes, and
5. Radiochemistry.

VOC samples were collected in two, 40-ml amber glass vials which contained 10 drops 1:1 hydrochloric (HCl) acid preservative prepared by the laboratory. Before sealing the vials with Teflon caps, litmus paper was used to make certain the pH of the sample was below 2 SU; additional HCl was added if necessary. VOC samples were also checked to make sure there was no headspace.

Pesticide samples were collected in two bottles: an unpreserved, one-gallon, amber glass container; and, for carbamates which break down at higher pH levels, a 60 ml glass container preserved with 1.8 ml monochloro (13.3 percent) - acedicitic acid (5.6 percent) and potassium hydroide (5.1 percent).

The inorganic constituents were collected in three, 1-liter polyethylene bottles:

< Samples to be analyzed for dissolved metals were filtered into bottles preserved with 5 mL nitric acid (70 percent). An on-site positive pressure filtering apparatus with a 0.45 micron (µM) pore size groundwater capsule filter was used,.

< Samples to be analyzed for nutrients were collected in bottles preserved with 2 ml sulfuric acid (95.5 percent), and

< Samples to be analyzed for other parameters were collected in unpreserved bottles.

Nitrogen isotope samples were collected in 1 liter unpreserved plastic bottles and were filled until no headspace remained.

Radiochemistry samples were collected in two, collapsible 1-liter plastic containers and preserved with 5 ml nitric acid to reduce the pH below 2.5 SU. All samples were kept at 4^0C with ice in an insulated cooler, with the exception of the radiochemistry samples.

Chain of custody procedures were followed in sample handling. Groundwater samples for this study were collected between June 1999 and November 1999.

Laboratory Methods

The inorganic and pesticide analyses for this study were conducted by the ADHS Laboratory in Phoenix, AZ, the only exception being inorganic splits analyzed by Del Mar Laboratory in Phoenix. A complete listing of inorganic parameters, including ADHS and Del Mar laboratory methods, EPA water method, and Minimum Reporting Levels (MRLs), is provided in **Table 4**. During sample collection, temperature, pH, and SC were recorded in the field.

VOC analyses for sites WCX-1 through 41 and WCX-74 were conducted by the ADHS Laboratory in Phoenix while WCX-42 through 72 were conducted by Del Mar Laboratory in Phoenix.

The SDW radiochemistry samples were analyzed by the Arizona Radiation Regulatory Agency (ARRA) laboratory in Phoenix except for one split analyzed by Lucas Laboratories of Sedona, AZ. The analysis of radiochemistry samples was treated according to the following SDW protocols.[4] Gross alpha and gross beta were analyzed, and if the gross alpha levels exceeded 5 pCi/L, then Radium-226 was measured. When radium-226 exceeded 3 pCi/L, radium-228 was measured. If gross alpha levels exceeded 15 pCi/L, then radium-226/228 and mass uranium were measured.

Nitrogen isotope samples were analyzed by the University of Illinois, Urbana, IL.

Sample Numbers

Fifty-eight (58) sites - wells and springs - were sampled for the study; 46 random sites and 12 targeted sites. Various numbers and types of samples were collected and analyzed:

< 58 - inorganics,
< 54 - VOCs,
< 52 - radiochemistry,
< 7 - Isotopes of hydrogen, and
< 4 - GWPL pesticides.

Table 4. ADHS / Del Mar Laboratory Methods Used for the WGB Study

Constituent	Instrumentation	ADHS / Del Mar Water Method	ADHS / Del Mar Minimum Reporting Level
Physical Parameters			
Alkalinity	Electrometric Titration	SM232OB	2 / 5
SC (FS/cm)	Electrometric	EPA 120.1 / SM2510B	1 / 2
Hardness	Titrimetric, EDTA	EPA 130.2 / SM2340B	10 / 1
pH (SU)	Electrometric	EPA 150.1	0.1
TDS	Gravimetric	EPA 160.1 / SM2540C	10 / 20
Turbidity (NTU)	Nephelometric	EPA 180.1	0.01 / 1
Major Ions			
Calcium (Ca)	ICP-AES	EPA 200.7	5 / 2
Magnesium (Mg)	ICP-AES	EPA 200.7	1 / 0.5
Sodium (Na)	ICP-AES	EPA 200.7 / EPA 273.1	5
Potassium (K)	Flame AA	EPA 258.1	0.5 / 1
Chloride (Cl)	Potentiometric Titration	SM 4500 CLD / EPA 300.0	1 / 5
Sulfate (SO_4)	Colorimetric	EPA 375.2 / EPA 300.0	10 / 5
Nutrients			
Nitrate as N (NO_3-N)	Colorimetric	EPA 353.2	0.02 / 0.50
Nitrite as N (NO_2-N)	Colorimetric	EPA 353.2	0.02
Ammonia (NH_3-N)	Colorimetric	EPA 350.1 / EPA 350.3	0.02 / 0.5
TKN	Colorimetric	EPA 351.2 / SM4500	0.05 / 0.5
Total Phosphorus	Colorimetric	EPA 365.4 / EPA 365.3	0.02 / 0.05

All units are mg/l except as noted
Source: ADHS Laboratory and Del Mar Laboratory

Table 4. ADHS / Del Mar Laboratory Methods Used for the WGB Study--Continued

Constituent	Instrumentation	ADHS / Del Mar Water Method	ADHS / Del Mar Minimum Reporting Level
		Trace Elements	
Antimony (Sb)	Graphite Furnace AA	EPA 200.9	0.005 / 0.004
Arsenic (As)	Graphite Furnace AA	EPA 200.9	0.01 / 0.003
Barium (Ba)	ICP-AES	EPA 200.7	0.1 / 0.01
Beryllium (Be)	Graphite Furnace AA	EPA 200.9	0.0005
Boron (B)	ICP-AES	EPA 200.7	0.1 / 0.5
Cadmium (Cd)	Graphite Furnace AA	EPA 200.9	0.001 / 0.0005
Chromium (Cr)	Graphite Furnace AA	EPA 200.9	0.01 / 0.004
Copper (Cu)	Graphite Furnace AA	EPA 200.9	0.01 / 0.004
Fluoride (F)	Ion Selective Electrode	SM 4500 F-C	0.20 / 0.1
Iron (Fe)	ICP-AES	EPA 200.7	0.1
Lead (Pb)	Graphite Furnace AA	EPA 200.9	0.005 / 0.002
Manganese (Mn)	ICP-AES	EPA 200.7	0.05 / 0.02
Mercury (Hg)	Cold Vapor AA	SM 3112 B / EPA 273.1	0.0005 / 0.0002
Nickel (Ni)	ICP-AES	EPA 200.7	0.1 / 0.05
Selenium (Se)	Graphite Furnace AA	EPA 200.9	0.005 / 0.004
Silver (Ag)	Graphite Furnace AA	EPA 200.9 / EPA 273.1	0.001 / 0.005
Thallium (Tl)	Graphite Furnace AA	EPA 200.9	0.002
Zinc (Zn)	ICP-AES	EPA 200.7	0.05

All units are mg/l
Source: ADHS Laboratory and Del Mar Laboratory

Appendix F. DATA EVALUATION

Quality Assurance

Quality assurance (QA) procedures were followed and quality control (QC) samples were collected to quantify data bias and variability for the WGB study. The design of the QA/QC plan was based on recommendations included in the *Quality Assurance Project Plan (QAPP)*[2] and the *Field Manual For Water Quality Sampling*.[7] The types and numbers of QC samples collected for this study are as follows:

Inorganic:	(8 duplicates, 2 splits, 6 blanks).
VOC:	(9 duplicates, 0 splits, 3 blanks).
Radiochemical:	(3 duplicates, 1 splits, 0 blanks).
Pesticide:	(0 duplicates, 0 splits, 0 blanks).
Nitrogen isotope:	(2 duplicates, 0 splits, 0 blanks).

Based on the QA/QC results which follow, sampling procedures and laboratory equipment did not significantly affect the groundwater quality samples.

Equipment Blanks - Equipment blanks were collected to ensure adequate decontamination of sampling equipment, and that the filter apparatus and/or deionized water were not impacting the samples. Equipment blank samples for major ion and nutrient analyses were collected by filling unpreserved and sulfuric acid preserved bottles with deionized water. Equipment blank samples for trace parameter analyses were collected with deionized water that had been filtered into nitric acid preserved bottles.

Systematic contamination was judged to occur if more than 50 percent of the equipment blank samples for a particular groundwater quality constituent contained measurable quantities of the constituent. As such, SC-lab and turbidity were considered to be affected by systematic contamination; however, the extent of contamination was not considered significant. Both SC and turbidity were detected in all six equipment blanks. SC had a mean level of 1.7 umhos/cm which was less than 1 percent of the SC median level for the study. The SC detections may be explained in two ways: water passed through a deionizing exchange unit will normally have an SC value of at least 1 FS/cm while carbon dioxide from the air can dissolve in deionized water with the resulting bicarbonate and hydrogen ions imparting the observed conductivity.[26] Similarly, turbidity had a mean level of 0.07 NTU, less than 1 percent of the turbidity median level for the study. Testing indicates turbidity is present at 0.01 NTU in the deionized water supplied by the ADHS laboratory, and levels increase with time due to storage in ADEQ carboys.[37] There were no detections of any compounds in the VOC travel blanks.

Duplicate Samples - Duplicate samples are identical sets of samples collected from the same source at the same time and submitted to the same laboratory. Data from duplicate samples provide a measure of variability from the combined effects of field and laboratory procedures. Duplicate samples were collected from sampling sites that were believed to have elevated constituent levels as judged by field SC values. Variability in constituent levels between each pair of duplicate samples is provided both in terms of absolute levels and as the percent difference. Percent difference is defined as the absolute difference between levels in the duplicate samples divided by the average level for the duplicate samples, multiplied by 100 (**Table 5**). Only constituents having levels exceeding the Minimum Reporting Level (MRL) were used in this analysis.

Analytical results indicate that of the 20 constituents examined, the maximum difference for the duplicate constituents rarely exceeded 10 percent while the median differences were within 4 percent except for turbidity (33 percent) and TKN (15 percent). Turbidity values can be impacted by the exceedance of this parameter's holding time; this occurred frequently during the study due to turbidity's short holding time.[37] TKN differences might be related to the analysis of this constituent, which is particularly difficult and sensitive.[37] Based on these results, the differences in constituent concentrations of duplicate samples were not considered to significantly impact the groundwater quality data.

Split Samples - Split samples are identical sets of samples collected from the same source at the same time that are submitted to two different laboratories to check for laboratory differences. Two inorganic split samples were collected. Analytical results from the split samples were evaluated by examining the variability in constituent levels in terms of absolute levels and as the percent difference. Of the constituent levels exceeding MRLs, all had less than 15 percent difference with the exception of turbidity, chloride, and sulfate. Based on these results, the differences in constituent levels of split samples were not considered to significantly impact the groundwater quality data.

Table 5. Summary Results of WGB Duplicate Samples from ADHS Laboratory

Parameter	Number	Difference in Percent			Difference in Concentrations		
		Minimum	Maximum	Median	Minimum	Maximum	Median
Physical Parameters and General Mineral Characteristics							
Alkalinity, Total	8	0 %	0 %	0 %	0	0	0
SC (FS/cm)	8	0 %	4 %	0 %	0	10	0
Hardness	8	0 %	3 %	0 %	0	10	0
pH-field (SU)	8	0 %	1 %	0 %	0	0.1	0
TDS	8	0 %	10 %	3 %	0	100	10
Turbidity (NTU)	8	0 %	145 %	33 %	0	0.27	0.1
Major Ions							
Bicarbonate	8	0 %	0 %	0 %	0	0	0
Calcium	8	0 %	4 %	1 %	0	2.0	0.2
Magnesium	8	0 %	8 %	0 %	0	1.0	0
Sodium	8	0 %	9 %	0 %	0	10.0	0
Potassium	8	0 %	8 %	0 %	0	0.1	0
Chloride	8	0 %	13 %	0 %	0	10.0	0
Sulfate	8	0 %	22 %	2 %	0	10.0	1.0
Nutrients							
Nitrate (as N)	8	0 %	4 %	0 %	0	0.1	0
TKN	4	7 %	15 %	15 %	0.008	0.01	0.009
Trace Elements							
Arsenic	4	0 %	3 %	0 %	0	0.002	0
Boron	4	0 %	0 %	0 %	0	0	0
Fluoride	8	0 %	10 %	1 %	0	0.2	0.06
Selenium	2	2 %	4 %	-	0.0001	0.0002	-
Zinc	3	0 %	5 %	4 %	0	0.01	0.003

All units are mg/l except as noted with certain physical parameters

Data Validation

The analytical work for this study was subjected to the following six QA/QC correlations.

Cation/Anion Balances - Cation/anion balance is an analysis such that, if found to be within acceptable limits, it can be assumed there are no important errors in concentrations reported for major ions.[26] Overall, cation/anion balances of WGB samples were significantly correlated (regression analysis, p # 0.01). All the cation/anion balances were within acceptable limits (90 - 110 percent) with the exception of seven samples, all which barely exceeded the acceptable limits. Many sample balances may have been altered by the non-detections of sulfate, which necessitated using an estimated sulfate concentration of ½ the MRL. Laboratory personnel indicated that other parameters not tested for, such as bromide and iodine, could have effected the cation/anion balances.[37]

SC/TDS - The SC and TDS concentrations measured by contract laboratories were significantly correlated as were field-SC and TDS concentrations (regression analysis, p # 0.01). Typically, the TDS concentration in mg/l should be from 0.55 to 0.75 times the SC in FS/cm for groundwater up to several thousand mg/l.[27] Groundwater in which the ions are mostly bicarbonate and chloride will have a factor near the lower end of this range and groundwater high in sulfate may reach or even exceed the upper end.[26] The relationship of TDS to SC becomes indefinite for groundwater both with very high and low concentrations of dissolved solids.[26]

Hardness - Concentrations of laboratory-measured and calculated hardness values were significantly correlated (regression analysis, p # 0.01). Hardness concentrations were calculated using the following formula: [(Ca x 2.497) + (Mg x 4.118)].

SC - The SC measured in the field using a Hydrolab at the time of sampling was significantly correlated with the SC measured by contract laboratories (regression analysis, p # 0.01).

pH - The pH value is closely related to the environment of the water and is likely to be altered by sampling and storage.[26] Even so, the pH values measured in the field using a Hydrolab at the time of sampling were significantly correlated with laboratory pH values (regression analysis, p # 0.01).

Groundwater Temperature/Groundwater Depth - Groundwater temperature measured in the field was compared to groundwater depth. Groundwater temperature should increase with depth, approximately 3 degrees Celsius with every 100 meters or 328 feet.[10] Groundwater temperature and well depth were significantly correlated (regression analysis, p # 0.01).

The analytical work conducted for this study was considered valid based on the quality control samples and the QA/QC correlations.

Statistical Considerations

Various methods were used to complete the statistical analyses for the groundwater quality data of this study. All statistical tests were conducted on a personal computer using SYSTAT software.[49]

Initially, data associated with 21 constituents were tested for both non-transformed and log-transformed normality using the Kolmogorov-Smirnov one-sample test with the Lilliefors option.[11] Results of this test using non-transformed data revealed that only bicarbonate, pH-field, temperature, and zinc were normally distributed. The distribution of many groundwater quality parameters is often not Gaussian or normal, but skewed to the right.

The results of the log-transformed test revealed that 16 of the 21 log-transformed constituents were normally-distributed. In summary, non-transformed data are overwhelmingly not normally-distributed while roughly three-quarters of the log-transformed constituents are normally-distributed. The most recent and comprehensive statistical references specifically recommend the use of non-parametric tests when the non-normality assumption is violated.[24]

Various aspects of WGB groundwater quality were analyzed using the following statistical methods:

Spatial Relationships: The non-parametric Kruskal-Wallis test was applied to investigate the hypothesis that constituent concentrations from groundwater sites in different groundwater aquifers, geologic types, and/or portions of the WGB were the same. The Kruskal-Wallis test uses the differences, but also incorporates information about the magnitude of each difference. The null hypothesis of identical median values for all data sets within each test was rejected if the probability of obtaining identical medians by chance was less than or equal to 0.05. Comparisons conducted using the

Kruskal-Wallis test include aquifers (*alluvial* and *hardrock*), portions of the basin (north and south), and geologic (*young alluvium*, *old alluvium*, *granite rock*, *metamorphic rock*, *volcanic rock*, and *sedimentary rock*). For geologic comparisons of six factors, if the null hypothesis was rejected for any of the tests conducted, the Tukey method of multiple comparisons on the ranks of the data was applied. The Tukey test identified significant differences between parameter concentrations when compared to each possibility within each of the tests.[24]

Both the Kruskal-Wallis and Tukey tests are not valid for data sets with greater than 50 percent of the constituent concentrations below the MRL.[24] Consequently, the Kruskal-Wallis test was not calculated for trace parameters such as antimony, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, as well as phenolphthalein alkalinity, nitrite, ammonia, and total phosphorus. Highlights of these statistical tests are summarized in the groundwater quality patterns section.

Groundwater Level Relationships: Simple regression was used to examine relationships between constituent concentrations and groundwater depth. Groundwater depth was determined using a sounder in the field when possible or obtained from well driller's logs. Comparisons were conducted using three distinct methods:

< Linear Model $[P] = md + b$ $[P]$ vs d
< Exponential Model $[P]_d = [P]_{d=0}e\text{-}rd$ $\ln[P]$ vs d
< Biphasic Model $[P] = a(d)\text{-}b$ $\ln[P]$ vs $\ln d$

The null hypothesis of no association between variables was rejected if the probability of obtaining the correlation by chance was less than or equal to 0.05. Significant correlations between the data sets are summarized in the groundwater quality patterns section.

Correlation Between Constituent Concentrations: In order to assess the strength of association between constituents, their various concentrations were compared to each other using the Pearson Correlation Coefficient test. The Pearson correlation coefficient varies between -1 and +1, with a value of +1 indicating that a variable can be predicted perfectly by a positive linear function of the other, and vice versa. A value of -1 indicates a perfect inverse or negative relationship.

The results of the Pearson Correlation Coefficient test were then subjected to a probability test to determine which of the individual pair wise correlations were significant.

The Pearson test is not valid for data sets with greater than 50 percent of the constituent concentrations below the MRL.[24] Consequently, Pearson Correlation Coefficients were not calculated for trace parameters such as antimony, arsenic, barium, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, as well as phenolphthalein alkalinity, nitrite, ammonia, and total phosphorus. Significant highlights from this statistical test are summarized in the groundwater composition section.

Time-Trend Analysis: Changes in constituent concentrations over time were examined utilizing data collected from the same wells by ADWR between 1987 and 1991 and ADEQ in 1999. The Wilcoxon rank-sum statistic, which is a non-parametric measure of association between two independent sets of data, was used to determine any significant changes in constituent concentrations between the different time periods.

The Wilcoxon test was used to test the null hypothesis that constituent concentrations collected in 1987-1991 were the same as constituent concentrations collected during 1999. The null hypothesis of identical median values for each data set was rejected if the probability of obtaining identical medians by chance was less or equal to 0.05.

The Wilcoxon test is not valid for data sets with greater than 50 percent of the constiutent concentrations below the MRL.[24] Consequently, the Wilcoxon test was not calculated for trace parameters such as antimony, arsenic, barium, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, as well as phenolphthalein alkalinity, nitrite, ammonia, and total phosphorus. Highlights from these statistical tests are summarized in the groundwater quality pattern section.